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DICTIONARY OF CHEMISTRY.

SECOND SUPPLEMENT.

**A S : S O C : B**

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A DICTIONARY  
OF  
CHEMISTRY

AND THE  
ALLIED BRANCHES OF OTHER SCIENCES.

BY  
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EDITOR OF  
'THE JOURNAL OF THE CHEMICAL SOCIETY.'

ASSISTED BY EMINENT CONTRIBUTORS.



SECOND SUPPLEMENT.



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## PREFACE.

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THIS SUPPLEMENT brings the Record of Chemical Discovery down to the end of the year 1872, including some of the more important discoveries which have appeared in 1873 and 1874.

The Author has much pleasure in stating that he has been favoured with the assistance of two of the former Contributors to the Dictionary, and of three other gentlemen, who have contributed articles of great interest and importance. The following is a list of the Contributors and of the Articles which they have written :—

H. E. ARMSTRONG, Ph.D., F.C.S., PROFESSOR OF CHEMISTRY AT THE LONDON INSTITUTION:

*Phenols.—Sulphur Chlorides.*

G. C. FOSTER, B.A., F.R.S., PROFESSOR OF PHYSICS AT UNIVERSITY COLLEGE:

*Magnetism.*

H. NEWELL MARTIN, M.B., D.Sc., B.A., FELLOW AND LECTURER OF CHRIST'S COLLEGE, CAMBRIDGE:

*Digestion.—Gastric Juice.—Glycogen.—Muscular Tissue.—Proteids, Respiration.—Urine.*

H. E. ROSCOE, Ph.D., F.R.S., PROFESSOR OF CHEMISTRY AT THE OWENS COLLEGE, MANCHESTER:

*Light, Chemical Action of.—Spectral Analysis.*

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*Fodder.—Maize.—Malt.—Manure.—Millet.—Oats.—Root-crops.*





# DICTIONARY OF CHEMISTRY.

## SECOND SUPPLEMENT.

### A

**ARIETENE.** A hydrocarbon obtained by distilling the resinous exudation of the nut-pine (*Pinus sabiniana*), indigenous in California. It has a specific gravity of 0.694 at 15°; distils almost constantly at about 101°; is nearly insoluble in water, but dissolves in 5 parts of alcohol of 95 p. c. It burns with a white smokeless flame, and dissolves fixed and volatile oils, except castor-oil. It has a pungent odour like that of orange-oil, and its vapour possesses powerful anæsthetic properties. It is attacked by boiling nitric acid, and gives substitution-products with chlorine. It has not been analysed (Wenzell, *Pharm. J. Trans.* [3] ii. 789).

**ARIETIC ACID.** See **COLOPHONY.**

**ACACIA.** The seeds of the *Acacia nilotica*, an arborescent leguminous plant, common in Egypt, have been examined by O. Popp (*Arch. Pharm.* [2] cxlv. 140). The tree produces innumerable leathery pods, which ripen in March. The ripe seeds are extremely hard and horny, but become soft by soaking in hot water. They are similar in composition to beans and peas, and might probably be used for food; in the dry state they yield from 5.3 to 5.5 p. c. nitrogen. The unripe pods give 1.8 to 2.0 p. c., the ripe pods 1.0 p. c. The ash of the seed has the following composition:—

K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>2</sup>	SrO <sup>2</sup>	Cl	CO <sup>2</sup>
33.39	5.36	14.21	12.10	0.61	16.23	3.65	1.81	0.35	12.11 = 99.82

**ACEDIAMINE.** This name was given by Strecker to a base the hydrochloride of which was said to be produced by the action of gaseous hydrogen chloride on fused acetamide (i. 2). Tawildkrow, however (*Deut. Chem. Ges. Ber.* v. 477), obtained by this reaction nothing but a mixture of sal-ammoniac and hydrochloride of diacetamide; neither did he succeed in forming acediamine by the action of sal-ammoniac on acetamide, or of ammonia or ammonium iodide on acetonitril.

**ACENAPHTHENE.** See **NAPHTHALENE.**

**ACETAL,**  $\text{CH}^2\text{—CH}(\text{OC}^2\text{H}^5)^2$ .—When bromine is added by drops to acetal in a cooled vessel, and the product washed with water and alkalis, a heavy, extremely pungent oil is obtained, which, when purified by fractional distillation, yields monobromacetal,  $\text{CH}^2\text{Br.CH}(\text{OC}^2\text{H}^5)^2$ . This compound in the pure state has a not unpleasant odour; it is insoluble in water, and boils, with slight decomposition, at 170°. Treated with alcoholic potash at 160°–180° for twelve hours, it is converted into hydroxyl-acetal, or glycolacetal,  $\text{CH}^2(\text{OH}).\text{CH}(\text{OC}^2\text{H}^5)^2$ , a colourless, fragrant liquid, boiling, without decomposition, at 167°. Vapour-density, obs. = 66.61 ( $\text{H} = 1$ ), calc. = 67.

Glycolacetal is completely destroyed at common temperatures by strong sulphuric acid and by gaseous hydrochloric acid; glacial acetic acid does not act upon it in the cold; but at 100° slight browning takes place, and at 120° the decomposition is complete in a few hours. The product contains a body which has the odour of aldehyde, gives a specular deposit with silver nitrate, and, when treated with hydrogen sulphide, forms oily drops having the characteristic smell of sulphaldehyde; but it has not been obtained in sufficient quantity for satisfactory investigation.

*Ethylie Glycolacetal*, or *Glycolacetal ether*,  $\text{CH}^2(\text{OC}^2\text{H}^5)^2.\text{CH}(\text{OC}^2\text{H}^5)^2$ , obtained by the action of a concentrated solution of sodium ethylate at 160° on bromacetal, is a

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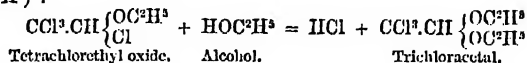
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liquid having an agreeable odour, boiling at  $164^{\circ}$ , and entirely destroyed by strong acids.

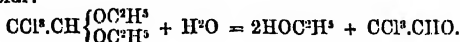
*Diethyl Glycolacetal*,  $\text{CH}(\text{OC}^2\text{H}^5)^2 \cdot \text{CH}(\text{OC}^2\text{H}^5)^2$ , corresponding to glyoxal, is obtained in like manner by the action of sodium ethylate on dichloroacetal; it boils at about  $180^{\circ}$  without decomposition, and is entirely destroyed by strong acids (Pinner, *Deut. Chem. Ges. Ber.* v. 147).

**Trichloroacetal**,  $\text{C}^1\text{H}^1\text{Cl}^3\text{O}$ .—Of this compound there are two modifications: one of which, solid at ordinary temperatures and melting at about  $72^{\circ}$ , was obtained by Paternò, in 1868, as a secondary product in the preparation of dichloroacetal by the action of chlorine upon alcohol (1st *Suppl.* 4); while the other, which is liquid at ordinary temperatures, is obtained by heating tetrachloroethyl oxide,  $\text{CCl}^3\text{CH}(\text{OC}^2\text{H}^5)\text{Cl}$ , with alcohol in sealed tubes (Wurtz a. Vogt, *Compt. rend.* lxxiv. 277.—Paternò a. Pisati, *Gazzetta chimica italiana*, ii. 333). This latter modification is a transparent, colourless liquid, having a pleasant odour, much like that of dichloroacetal, boiling at  $199^{\circ}$ – $201^{\circ}$  (Wurtz a. Vogt); at  $204.8^{\circ}$  (corr.), under a pressure of 758.9 mm. Sp. gr. 1.2813 at  $0^{\circ}$ ; 1.2655 at  $22.2^{\circ}$ ; 1.617 at  $99.96^{\circ}$  (Paternò a. Pisati).

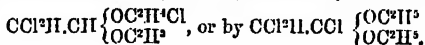
The mode of formation of the liquid trichloroacetal shows that it has the constitution  $\text{CCl}^3\text{CH}(\text{OC}^2\text{H}^5)^2$ :



which is confirmed by the mode of decomposition of the compound when heated with water or with sulphuric acid, the products of which, according to Wurtz a. Vogt, are alcohol and chloral:



The solid trichloroacetal appears also to yield chloral when heated with sulphuric acid; at all events, the distillate, when heated with potash and a small quantity of aniline, gives off the characteristic odour of the carbamides (isocyanides), a result which indicates the formation of chloroform, and thereby tends to show that the product of the action of sulphuric acid on trichloroacetal is really chloral. Nevertheless, Paternò a. Pisati do not regard their experiments (which were made on a small quantity of substance) as quite conclusive on this point, but think it possible that the product of this reaction may be dichloraldehyde,  $\text{C}^2\text{Cl}^2\text{H}_2\text{CHO}$ . In this case, the constitution of solid trichloroacetal might be represented by the formula:

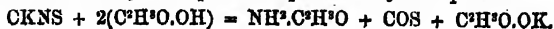


Tetrachloroethyl oxide is transformed into trichloroacetal, not only by alcohol, but likewise, though much less completely, by sodium ethylate, or a very strong alcoholic solution of potash. If, however, the same compound be treated with a 10 p. c. solution of potassium hydrate in absolute alcohol, a totally different reaction takes place, a molecule of hydrochloric acid being eliminated, and a compound being formed which appears to have the constitution  $\text{CCl}^2\text{—CCl—OC}^2\text{H}^5$ . The reaction takes place at ordinary temperatures, with abundant deposition of potassium chloride. On dissolving out this salt by water, an oily liquid separates, which, when dried and purified by fractional distillation, boils at  $154.8^{\circ}$  (corr.) under the pressure of 755 mm., has a density of 1.5725 at  $0^{\circ}$  and 1.2354 at  $99.9^{\circ}$ , and gives by analysis 26.45 to 27.53 p. c. carbon, 2.93 to 2.98 hydrogen, and 59.55 to 60.59 chlorine; the formula  $\text{C}^1\text{H}^1\text{Cl}^2\text{O}$  requiring 27.35 p. c. C., 2.85 H. and 60.68 Cl.

This compound unites directly with *bromine*, the combination being attended with rise of temperature, and forms a liquid which, after washing with water and sodium carbonate, is perfectly colourless; it is much heavier than water, is decomposed by distillation under ordinary pressure, but distils without alteration under a pressure of 4 centimeters, and boils at about  $135^{\circ}$ ; in a mixture of snow and salt it solidifies to a crystalline mass which melts at the temperature of the air.

This chlorobrominated compound probably has the constitution represented by the formula  $\text{CCl}^2\text{Br—CClBr.O.C}^2\text{H}^5$ . It is violently attacked by concentrated alcoholic potash, yielding a heavy oil, which may be separated by distillation with aqueous vapour into the original chlorinated compound, and a substance which is solid at the ordinary temperature ( $24^{\circ}$ ), and well crystallised (Paternò a. Pisati).

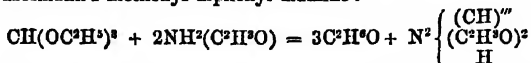
**ACETAMIDE**.  $\text{C}^2\text{H}^3\text{ONH}^2$ .—This compound is formed when acetic acid is boiled with potassium sulphocyanate; but prolonged heating is necessary to complete the reaction, which mainly takes place as represented by the equation:



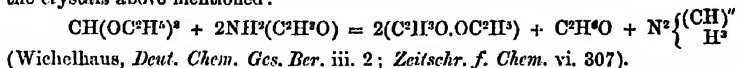
At the same time, however, acetonitril, carbon dioxide and hydrogen sulphide are formed in small quantity by a secondary reaction (Letts, *Deut. Chem. Ges. Ber.* v. 669).

Acetamide is easily converted into acetonitril,  $C^2H^3N$ , by the action of *phosphorus pentasulphide*. The decomposition begins at ordinary temperatures, but heat is required to complete it. Hydrogen sulphide is given off, and a blackish tumented mass remains in the retort. Similar reactions take place with other amides (L. Henry, *Compt. rend.* lxxiii. 1273).

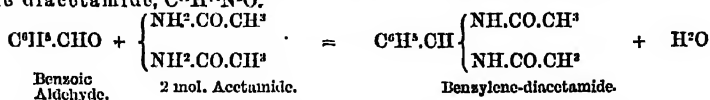
When acetamide is heated to  $180^\circ$  in sealed tubes with *orthoformic ether*, alcohol is formed, together with needle-shaped crystals of methenyl-diacetyl-diamino, a base analogous to Hofmann's methenyl-diphenyl-diamino:



At the same time another reaction takes place, yielding acetic ether and methenyl-diamino,  $CH^3N^2$ , which may be separated as a platinum salt from the mother-liquor of the crystals above mentioned:



Acetamide heated in sealed tubes with *benzoic aldehyde* is converted into benzylene diacetamide,  $C^{11}H^{11}N^2O$ .



(E. Roth, *Zeitschr. f. Chem.* [2] vi. 680).

A precisely similar reaction takes place with *acetic aldehyde*, yielding the compound  $C^{11}H^{11}.CH(NH.C^2H^3O)^2$ , which crystallises in large prisms melting at  $169^\circ$  and distilling with partial decomposition. On heating it with acids, the aldehyde is set free (Tawildarow, *Deut. Chem. Ges. Ber.* v. 477).

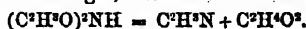
Acetamide heated for some time to  $128^\circ$ – $180^\circ$  with *anisaldehyde*, yields a compound,  $C^{12}H^{12}.N^2O^2$ , which forms nodular groups of needles melting at  $180^\circ$ , soluble in water, insoluble in alcohol and ether, decomposed by hydrochloric acid, with separation of anisaldehyde, not altered by potash-ley, even at boiling heat (A. Schuster, *Zeitschr. f. Chem.* [2] vi. 681).

Acetamide heated with *salicylot* in various proportions, yields a yellow neutral substance insoluble in alcohol, and containing, after washing with alcohol, from 63.3 to 68.5 p.c. carbon, and 5.7 to 8.1 hydrogen; it is soluble in aqueous and alcoholic potash, and hydrochloric acid added to the solution throws down a reddish-brown spongy substance. Strong hydrochloric acid decomposes it with red coloration (B. Credner, *Zeitschr. f. Chem.* [2] vi. 80).

Acetamide unites directly with *chloral*, forming the crystalline compound  $C^2H^3NO$ .  $CHCl^3O$ . (See *CHLORAL*).

When acetamide is heated with *sodium ethylate*, both being perfectly dry, ammonia is given off, and a crystalline residue is left, which is decomposed by water, yielding ammonia and acetate of sodium. When a solution of acetamide in slightly warm, absolute alcohol is added to a cold viscid solution of sodium ethylate, large plates of sodium ethylate are deposited, enclosing feathery crystals of acetamide (W. N. Hartley, *Chem. Soc. J.* [2] xi. 991).

*Diacetamide*,  $(C^2H^3O)^2NH$ , is formed by heating equivalent quantities of acetonitril and acetic acid to  $250^\circ$ , or by heating acetamide with acetic anhydride to  $250^\circ$  for six hours. It melts at  $59^\circ$ – $60^\circ$ , and boils at  $215^\circ$ . By heating with zinc chloride it is resolved, without evolution of gas, into acetonitril and acetic acid:



(Linnemann, *Wien. Akad. Ber.* lx. [2] 44; *Jahresb.* 1869, p. 601).

According to Wichelhaus (*Deut. Chem. Ges. Ber.* iii. 847; *Chem. Soc. J.* [2] ix. 407), triacetamide is also formed in small quantity when a mixture of acetic anhydride and acetonitril is heated above  $200^\circ$ , and may be dissolved out by ether, after the excess of acetic anhydride has been removed by distillation. It crystallises in small white flexible needles, very much like diacetamide, and melts at  $78^\circ$ – $79^\circ$  (diacetamide at  $74^\circ$ – $75^\circ$ , acetamide at  $78^\circ$ ). Diacetamide and acetamide treated with silver oxide in the cold, dissolve and form peculiar salts; whereas triacetamide at first forms no such compound; when gently warmed, however, all three yield silver acetate. Acetamide retains its odour when dissolved; diacetamide, under

the same circumstances, gives an acid reaction, and triacetamide is neutral. Diacetamide-treated with phosphoric anhydride, yields acetoneitril and acetic acid or anhydride.

*Chlorinated Acetamides* are prepared by allowing the ethylic ether of the corresponding chloroacetic acid to remain for some days in contact with aqueous ammonia. The amides thus produced are but slightly soluble in water, their solubility decreasing as the degree of chlorination becomes greater. By distillation with phosphoric anhydride they are converted into the corresponding chloroaceto-nitrils: e.g.  $\text{C}^2\text{HCl}^2\text{O.NH}^2 - \text{H}^2\text{O} = \text{C}^2\text{HCl}^2\text{N}$  (L. Bisschoppinck, *Deut. Chem. Ges. Ber.* vi. 731).

*Monochloroacetamide*,  $\text{C}^2\text{H}^2\text{ClO.NH}^2$ , melts at  $116^\circ$ , and when subjected to a pressure of 743 mm. boils, with partial decomposition, at  $224^\circ$ – $225^\circ$  (Bisschoppinck). According to Menschutkin a. Jermolowew (*Zeitschr. f. Chem.* [2] vii. 5), it crystallises in thick prisms, easily soluble in alcohol and water, especially when boiling. It melts at  $119.5^\circ$  and solidifies at about  $116^\circ$ ; sublimes very easily, even at the temperature of the water-bath, in broad, large needles; and distils in very small quantity, apparently undecomposed. Alkalis and baryta-water readily evolve ammonia from it on warming.

The *mercury-compound*,  $(\text{C}^2\text{H}^2\text{ClO.NH})^2\text{Hg}$ , is formed by adding precipitated mercuric oxide to an aqueous solution of chloroacetamide so long as the colour changes to white, then adding a large quantity of water, boiling, filtering, and exhausting the residue with boiling water. The air-dried compound does not lose weight over oil of vitriol, but begins to decompose at  $100^\circ$ . The compound is deposited from solution in fine needles or in warty masses made up of small needles. It dissolves with great difficulty in boiling water, and is nearly insoluble in cold water. When it is heated to  $170^\circ$ , a violent reaction occurs; chloroacetamide sublimes, and mercury and carbon are left behind. The *silver-compound* cannot be obtained on account of its instability (Menschutkin a. Jermolowew).

*Dichloroacetamide*,  $\text{C}^2\text{HCl}^2\text{O.NH}^2$ , melts at  $96^\circ$ , and, under a pressure of 745 mm., distils without change at  $233^\circ$ – $234^\circ$ . *Trichloroacetamide*,  $\text{C}^2\text{Cl}^3\text{O.NH}^2$ , melts at  $136^\circ$  and boils at  $238^\circ$ – $239^\circ$  under a pressure of 476 mm. (Bisschoppinck).

*Iodoacetamide*,  $\text{C}^2\text{H}^2\text{IO.NH}^2$ , is obtained by treating an alcoholic solution of chloroacetamide with solid potassium iodide for a day at the ordinary temperature, with frequent agitation, and then evaporating the alcoholic solution. The amide crystallises from water, in which it is easily soluble, in fine colourless opaque prisms. When heated it melts, turns yellow, and decomposes, evolving fumes of iodine (Menschutkin a. Jermolowew).

*Ethylacetamide*,  $\text{C}^2\text{H}^3\text{O.NHC}^2\text{H}^5$ , obtained by dehydration of ethylamine acetate, boils at  $203^\circ$ – $204^\circ$ , and is resolved by fusion with zinc chloride into carbon monoxide, hydrocarbons, and ammonia (Linneemann).

*Phenyl-acetamide*, or *Acetanilide*,  $\text{C}^2\text{H}^5\text{O.NHC}^6\text{H}^5$ , prepared from pure aniline and glacial acetic acid, crystallises in very thin rhombohedral laminae, melting between  $112^\circ$  and  $113^\circ$ . It is easily decomposed by boiling dilute sulphuric acid, with formation of acetic acid and aniline sulphate.

To detect *tolylacetamide* (acetoluide) in acetanilide, the compound may be dissolved in 4 parts glacial acetic acid and the liquid diluted with about 80 parts of water, whereupon nearly all the acetanilide remains dissolved, while the acetoluide separates and may be purified by a second crystallisation from a small quantity of glacial acetic acid, or by one or two crystallisations from hot water. Acetoluide melts at a temperature above  $140^\circ$  (Merz a. Weith, *Zeitschr. f. Chem.* [2] v. 699).

*Sodium-acetanilide*,  $\text{C}^6\text{H}^5\text{NaNO}$ , is produced by the action of sodium on a hot solution of acetanilide in xylene (Bunge, *ibid.* vi. 119).

#### ACETAMIDE-CHLORAL. See CHLORAL.

**ACETIC ACID**,  $\text{C}^2\text{H}^4\text{O}^2$ .—*Formation*.—1. By direct oxidation of acetylene. When a mixture of 1 vol. acetylene and 20 vols. air is exposed to diffused daylight at ordinary temperatures in contact with dilute potash-solution, the greater part of the acetylene disappears in the course of six months, together with a volume of oxygen equal to half that of the acetylene, and about half the acetylene thus consumed is converted into acetic acid:  $\text{C}^2\text{H}^2 + \text{O} + \text{KHO} = \text{C}^2\text{H}^3\text{KO}^2$ , the remainder being condensed to a bituminous substance, also containing carbon, hydrogen, and oxygen.—The conversion of the acetylene into acetic acid is more complete when pure chromic acid is used as the oxidising agent. If only a little water is present, the reaction is sudden, violent, and attended with considerable evolution of heat, the products being carbonic, formic, and a variable quantity of acetic acid. To obtain the acetic acid

pure chromic anhydride must be added to an aqueous solution of acetylene, and the solution left to itself at the temperature of the air. The liquid then gradually turns brown and the acetylene disappears, and on distilling and saturating the distillate with barium carbonate, perfectly pure barium acetate is obtained (Berthelot, *Compt. rend.* lxx. 256; *Ann. Ch. Phys.* [4] xxiii. 212).—2. Together with carbonic acid, when essential oil of orange-peel is oxidised by boiling with a mixture of potassium dichromate and sulphuric acid (Wright a. Piesse, *Chem. Soc. J.* [2] ix. 118, 7).—3. Together with several of its homologues, by saponifying croton-oil with caustic soda (Gauthier a. Fröhlich, *Zeitschr. f. Chem.* [2] vi. 549).

**Solidification.**—Glacial acetic acid melts at  $16.7^{\circ}$ , and boils under the normal atmospheric pressure at  $117.8^{\circ}$ . By slow cooling it may be cooled to  $10^{\circ}$ – $8^{\circ}$  without solidifying even on agitation. Solidification, however, takes place immediately when a granule of the solid acid is thrown into the liquid cooled to below  $16.7^{\circ}$ , the temperature at the same time rising to  $16.7^{\circ}$ . If the solidified acid be slowly fused by immersing the vessel in water of about  $25^{\circ}$ , an immersed thermometer exhibits the temperature of  $16.7^{\circ}$  so long as any considerable quantity of the solid acid remains unmelted: the melting and solidifying points of the glacial acid are therefore identical.

When a mixture of glacial acetic acid and water is cooled, it does not solidify as a whole, but the acetic acid crystallises out, leaving the water liquid, just as a salt separates on cooling from a saline solution. In determining the solidifying point of aqueous acetic acid of given strength, it is necessary—since the separation of a large quantity of acetic acid would alter the proportion between the acid and water—to take care that only a small portion of acetic acid separates out. The best way of ensuring this condition is to cool the liquid about a degree below the approximately determined solidifying point, then throw in a granule of the glacial acid, and stir with a delicate thermometer. The temperature then rises to the solidifying point of the mixture. The results of experiments made in this manner are given in the following table:—

100 parts, by weight, of Acetic Acid mixed with :	100 parts, by weight, of the mixture contain :	Temperature of Solidification :
0.0 Water,	0.0 Water.	$16.7^{\circ}$ C.
0.5 "	0.497 "	$15.65$
1.0 "	0.990 "	$14.8$
1.5 "	1.477 "	$14.0$
2.0 "	1.961 "	$13.25$
3.0 "	2.912 "	$11.95$
4.0 "	3.846 "	$10.5$
5.0 "	4.761 "	$9.4$
6.0 "	5.660 "	$8.2$
7.0 "	6.542 "	$7.1$
8.0 "	7.407 "	$6.25$
9.0 "	8.257 "	$5.3$
10.0 "	9.090 "	$4.3$
11.0 "	9.910 "	$3.6$
12.0 "	10.774 "	$2.7$
15.0 "	13.043 "	$0.2$
18.0 "	15.324 "	$2.6$
21.0 "	17.355 "	$5.1$
24.0 "	19.354 "	$7.4$

This table shows that the proportion of acetic acid, especially in the more highly concentrated aqueous acid, may be determined, by means of the solidifying point, to within 1–10th p.c.—a degree of accuracy not attainable by any other method yet proposed. Other substances act like water in lowering the solidifying point of acetic acid, e.g. sulphuric acid, alcohol, and certain salts which dissolve in the acid. From a mixture of 100 parts acetic acid ( $C^2H^4O^2$ ) and 0.5 sulphuric acid ( $H^2SO^4$ ), the acetic acid solidifies at  $16.4^{\circ}$ ; from a mixture of 100 acetic acid and 1.8 alcohol, at  $15.25^{\circ}$ . The action of water may, however, be partly counteracted by addition of sulphuric acid. Thus, from a mixture of 100 parts acetic acid and 10 parts water, the acetic acid separates at  $4.3^{\circ}$ ; but if 2 parts of sulphuric acid are added, solidification takes place at  $5.8^{\circ}$ ; and from a mixture of 100 acetic acid, 10 water, and 20 sulphuric acid, the acetic acid solidifies at  $10.7^{\circ}$ .

The solidification of pure acetic acid may be exhibited with certainty, even in summer; namely, by immersing the vessel in cold water at about  $10^{\circ}$  or  $12^{\circ}$ , throwing in a fragment of the glacial acid, and agitating, whereupon the acid immediately

solidifies. A small quantity of the solid acid is very easily obtained by stirring a mixture of cold water and sal-ammoniac ammonium nitrate, or potassium sulphocyanate, with a test-tube containing a few drops of the liquid acid. The low temperature thereby produced causes the acetic acid to solidify (F. Rüdorff, *Deut. Chem. Ges. Ber.* iii. 390).

*Vapour-density.*—Horstmann (*Deut. Chem. Ges. Ber.* iii. 78) has determined the density of saturated acetic acid vapour by calculations based upon the weight of acetic acid which can be taken up by an uncondensable gas at a given temperature. Let  $V$  be the volume of the gas at  $0^\circ$  and 760 mm. At the temperature  $t^\circ$  and barometric pressure  $P$ , this volume, after the gas has become saturated with acetic acid, vapour of tension  $p$ , becomes

$$V = V_0 \cdot \frac{273+t}{273} \cdot \frac{760}{p}$$

$V$  is also the volume of the vapour taken up at  $t$  under the partial pressure  $p$ . If, then,  $d$  denotes the specific gravity of this vapour, its weight  $W$  will be given by the formula :

$$W = V \cdot \frac{273}{273+t} \cdot \frac{p}{760} \cdot 0.001293 d$$

$$= V_0 \cdot \frac{p}{P-p} \cdot 0.001293 d$$

$$\text{whence } d = \frac{W(P-p)}{V_0 \cdot p \cdot 0.001293}$$

The mode of experimenting was as follows:—A measured volume of dry air was passed first through a flask containing acetic kept at a temperature somewhat above that at which the observation was to be made, then through a long tube containing glass beads moistened with acetic acid. This tube was laid in a large water-bath with several walls, the temperature of which could easily be regulated and kept constant. The temperature of the stream of gas was measured at the point where the gas, while still within the bath, passed over into the absorption apparatus, where the acetic acid was taken up by potash. Any water-vapour that might be given off from the potash solution was stopped by calcium chloride. In calculating the results of the experiments, the determinations of the vapour-tension of acetic acid made by Landolt (*Ann. Ch. Pharm. Suppl.* vi. 157) were made use of. These determinations refer to acetic acid evaporating in a vacuum, whereas Horstmann's refer to evaporation in air; but direct experiments showed that the errors thence arising were inconsiderable.

*Density of Saturated Acetic Acid Vapour.*

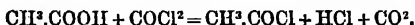
Temperature	Tension	Density	Temperature	Tension	Density
12.4°	13.5 mm.	1.89	27.6°	26.5 mm.	2.46
12.7	13.7	1.96	33.3	33.4	2.58
14.7	15.1	1.78.	38.5	41.5	2.72
15.6	15.6	1.98	38.5	41.5	2.79
17.4	16.8	2.09	41.6	53.1	2.75
20.2	19.0	2.28	48.7	63.0	2.98
21.5	20.4	2.24	51.1	69.0	3.16
22.6	21.2	2.29	59.9	97.0	3.72
25.0	23.5	2.42	62.9	109.2	3.11
26.1	25.0	2.32	63.1	100.0	3.19

Hence it appears that for a pressure of about 20 mm., acetic acid has, even at ordinary temperatures, nearly its normal density (2.08). The lower values obtained in a few cases arise from uncertainty in the measurement of the tension. Below  $17^\circ$  the results were vitiated by the solidification of the acetic acid, and above  $60^\circ$  constancy of temperature could not be effectually maintained. For the boiling point ( $120^\circ$ ) Horstmann, from former experiments (*Ann. Ch. Pharm. Suppl.* vi. 66), had estimated the density of saturated acetic acid vapour at about 3.3. It does not therefore appear to increase much after  $60^\circ$ .

A. Naumann has also examined the vapour-density of acetic acid vapour with the following results:—1. At a constant temperature the quantities of acetic acid contained in the unit of volume increase in greater proportion than the pressures.—2. The density of

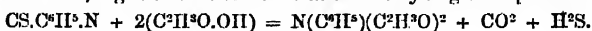
acetic acid vapour, referred to that of air at the same pressure and temperature, decreases for a given quantity of the vapour in the unit of volume, as the temperature rises. Now, as this density must be the same for different temperatures if the vapour of acetic acid at those different temperatures were composed of similar molecules, it follows from the second of the preceding propositions: 3. That the molecules of acetic acid vapour are not similarly constituted at all temperatures, but that a given quantity of acetic acid forms a smaller number of molecules at low than at high temperatures.—4. It must also be supposed that, as the mean distances between the molecules increase, the attraction between them likewise diminishes (*Ann. Ch. Pharm.* clv. 325); (*Deut. Chem. Ges. Ber.* iii. 702).

**Reactions.**—Acetic acid and phosgene act on one another at 110–120°, producing acetyl chloride:



(Kempff, *J. pr. Chem.* [2] i. 402.)

Acetic acid heated under pressure to 130°–140° with *phenyl sulphocyanate*, forms phenyl-diacetamido, together with carbon dioxide and hydrogen sulphide:



(Hofmann, *Deut. Chem. Ges. Ber.* iii. 770.)

When acetic acid and *benzoic aldehyde* are heated in a sealed tube to 160°, the tube then opened and hydrochloric acid gas passed into the liquid, or zinc chloride added to it, the sides of the tube become covered with small shining crystals of cinnamic acid, another portion of which remains in solution:



The quantity of cinnamic acid thus obtained is, however, but small, part of it being decomposed by the further action of the hydrochloric acid or zinc chloride, with formation of metacinnamone (Schiff, *Deut. Chem. Ges. Ber.* iii. 412).

**Metallic Acetates.** Respecting the action of acetates upon lead-salts, see LEAD.

**Potassium Acetate**, decomposed by the electric current, yields at the positive pole—besides dimethyl or ethane, and carbon dioxide—ethylene (formerly mistaken for methyl oxide, i. 17) and a mixture of the vapours of methyl formate, acetate, and carbonate, which condense when the dried gaseous mixture is passed through a tube cooled by a freezing mixture. The ethylene appears to be formed by oxidation of the ethane, according to the equation  $\text{C}^2\text{H}^4 + \text{O} = \text{C}^2\text{H}^2 + \text{H}^2\text{O}$ . The hydrogen evolved at the negative pole burns with a distinctly luminous flame, possibly due to the presence of traces of acetylene (Kempt & Kolbe, *J. pr. Chem.* [2] iv. 46).

**Sodium Acetate.**—When crystallised sodium acetate,  $\text{C}^2\text{H}^3\text{NaO}_2 + 3\text{H}^2\text{O}$ , is melted in a flask and the liquid heated to its boiling point (120°–123°), the flask closed with cotton-wool while the liquid is boiling, and then left to cool, crystallisation takes place when the liquid is nearly cold, the crystals, when drained from the mother-liquor, having the composition  $2\text{C}^2\text{H}^3\text{NaO}_2 + 5\text{H}^2\text{O}$ . These crystals melt at about 126°, and the liquid on cooling yields crystals which, after draining, consist of the monohydrate,  $\text{C}^2\text{H}^3\text{NaO}_2 + \text{H}^2\text{O}$ . Sodium acetate, melted and boiled for a few seconds only, yielded, on cooling, crystals, which gave by analysis numbers agreeing with the formula  $4\text{C}^2\text{H}^3\text{NaO}_2 + 9\text{H}^2\text{O}$ ; and by a second melting crystals were formed containing  $4\text{C}^2\text{H}^3\text{NaO}_2 + 5\text{H}^2\text{O}$  (Zettnow, *Pogg. Ann.* cxlii. 306).

When an aqueous solution of sodium acetate turns mouldy, oxygen is absorbed and a small quantity of alcohol is formed. A solution of 300 grains of pure crystallised sodium acetate, left to itself from Feb. 4, 1864, to May 20, 1868, had lost 6·85 grains of acetic acid, and yielded 0·6 cub. cent. of (pure) alcohol. A small quantity of formic acid was also produced (Béchamp, *Zeitschr. f. Chem.* vi. 438).

**Uranium Acetates.**—*Uranio-cobaltous acetate*,  $\text{Co}''(\text{C}^2\text{H}^3\text{O}_2)^2 \cdot 2(\text{UO}^2)'(\text{C}^2\text{H}^3\text{O}_2)^2 + 6 \text{ aq.}$ , forms small yellow-brown dimetric crystals, which at 130° give off all their water and turn violet (Rammelsberg, *Pogg. Ann.* cxlv. 158).

*Uranio-cuprio Acetate*,  $\text{Cu}''(\text{C}^2\text{H}^3\text{O}_2)^2 \cdot 2(\text{UO}^2)'(\text{C}^2\text{H}^3\text{O}_2)^2 + 4 \text{ aq.}$ , is precipitated from a mixture of the two salts in green crystals belonging to the hexagonal system (Rammelsberg).

**Alcoholic Acetates.** *Acetio Ethers.*—*Ethyl Acetate.*—The statement of Wanklyn (1st Suppl. 16) that the action of sodium on ethyl acetate is not accompanied by evolution of hydrogen, is corroborated by the experiments of Ladenburg (*Deut. Chem. Ges. Ber.* iii. 305). He finds that acetic ether prepared in the ordinary way, then left for several weeks over calcium chloride, and distilled over recently fused calcium chloride

—whereupon it passes over at  $72^{\circ}$ – $74^{\circ}$ —is not pure, inasmuch as when heated in sealed tubes to  $200^{\circ}$ , and then distilled, it leaves a residue which boils above  $80^{\circ}$ , has a sour taste, a distinct odour of vinegar, and effervesces with sodium carbonate. Acetic ether, purified in the ordinary way, is attacked by silicium chloride only on first contact, and the mixture may then be heated to  $120^{\circ}$  without any further action taking place. Acetic ether which is no longer altered by silicium chloride is likewise not attacked by (metallically bright) sodium at ordinary temperatures, and only a few white specks are observed on the sodium even after several hours' boiling. When sodium is heated to  $100^{\circ}$  in a flask with acetic ether (purified as above, and freed by distillation from the greater part of the silicium chloride), the action begins only after several hours' heating, and only once in several experiments was a very small quantity of combustible gas obtained. Acetic ether freed from water and alcohol by means of phosphorous trichloride is likewise not attacked by sodium till heated nearly to  $100^{\circ}$ , and no gas is evolved. Hence it is inferred that the action of sodium on acetic ether takes place only at a temperature much higher than is generally supposed, and is not attended with evolution of hydrogen.

*Tribasic Acetic Ether*,  $\text{C}^3\text{H}^3(\text{OC}^2\text{H}^3)^3$ , is formed when sodium ethylate, free from alcohol, is mixed with the calculated quantity of dichloroethyl chloride,  $\text{C}^2\text{H}^2\text{Cl}^2$  (boiling at  $72^{\circ}$ – $75^{\circ}$ ), and a volume of anhydrous ether at least equal to that of the sodium ethylate, and heated to  $100^{\circ}$ – $120^{\circ}$  in a sealed tube till the solid sodium ethylate is converted into pulverulent sodium chloride (in about 12 hours). On opening the tube a gas escaped, probably  $\text{C}^2\text{H}^2\text{Cl}$ , and on dissolving out the sodium salts with water, shaking the ethereal layer with twice its volume of water, drying with calcium chloride, and distilling, there were obtained—together with ordinary acetic ether—*monochloroethyl-ethylene*,  $\text{C}^2\text{H}^2\text{Cl}(\text{OC}^2\text{H}^2)^2$ , boiling at about  $123^{\circ}$ , and *tribasic acetic ether*,  $\text{C}^2\text{H}^2(\text{OC}^2\text{H}^2)^3$ , boiling at  $142^{\circ}$ .

The monochloroethylene (not quite pure) had a specific gravity of 1.02 at  $22^{\circ}$ . It is a colourless combustible liquid, insoluble in water, and having a peculiar agreeable odour.

The tribasic acetic ether, still containing 10.2 p. c. of monochloroethyl-ethylene, had a sp. gr. of 0.94 at  $22^{\circ}$ . It is a colourless combustible liquid, having a peculiar agreeable, ethereal odour, not like that of ordinary ethyl acetate. Heated with water to  $120^{\circ}$ – $130^{\circ}$ , it is decomposed into alcohol and acetic acid (Genther, *Jenaische Zeitschrift*, iv. 221; *Jahresb.* 1870, 636).

*Propyl Acetate (normal)*,  $\text{C}^3\text{H}^4\text{O}^2 = \text{CH}^3\text{CH}^2\text{CH}^3.\text{C}^2\text{H}^3\text{O}^2$ , obtained by digesting the iodide with silver acetate, boils at  $102^{\circ}$  (bar. at 750 mm.), and has a specific gravity of 0.913 at  $0^{\circ}$  (Rossi, *Ann. Ch. Pharm.* clix. 79).

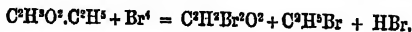
*Amyl Acetate (normal)*,  $\text{C}^5\text{H}^{10}\text{O}^2 = \text{CH}^3\text{CH}^2\text{CH}^2\text{CH}^2\text{CH}^3.\text{C}^2\text{H}^3\text{O}^2$ , was prepared by mixing normal amyl iodide with silver acetate and glacial acetic acid in a flask cooled with ice, the reaction which takes place spontaneously on removing the vessel from the ice-bath being completed by application of a gentle heat. The resulting amyl acetate, after purification in the usual way, had a sp. gr. of 0.8963 at  $0^{\circ}$ , 0.8793 at  $20^{\circ}$ , 0.8635 at  $40^{\circ}$ , and boiled at  $148.4^{\circ}$  (observed: correction for mercury-column =  $0.75^{\circ}$ ) under a barometric pressure of 737 mm. (Lieben u. Rossi, *Ann. Ch. Pharm.* clix. 70).

*Tolylene Acetate*,  $\text{C}^6\text{H}^4(\text{C}^2\text{H}^3\text{O}^2)^2$ , produced by heating an alcoholic solution of sodium acetate with tolylene chloride to  $150^{\circ}$ , forms hard shining laminae, having a hot camphorous taste, easily soluble in alcohol and ether. By distillation it appears to yield the monoacetate (Grignaux, *Compt. rend.* lxx. 1363).

#### Substitution-derivatives of Acetic Acid.

*Bromacetic Acid*,  $\text{C}^2\text{H}^3\text{BrO}^2$ , is formed when monobromacetylene, mixed with an indifferent gas, comes in contact with moist air, or when its alcoholic solution is exposed to the air:  $\text{C}^2\text{HBr} + \text{H}^2\text{O} + \text{O} = \text{C}^2\text{H}^3\text{BrO}^2$ .

*Dibromacetic Acid*,  $\text{C}^2\text{H}^2\text{Br}^2\text{O}^2$ , is produced by the action of bromine on ethyl acetate at  $130^{\circ}$ , much more easily than by treating acetic acid with bromine. The reaction is:



(Carius, *Deut. Chem. Ges. Ber.* iii. 336.)

*Chloracetic Acid*,  $\text{C}^2\text{H}^3\text{ClO}^2$ .—This acid, when heated with water, gradually decomposes, the more quickly as the quantity of water is greater and the temperature higher. A solution of the acid containing 0.324 gram  $\text{C}^2\text{H}^3\text{ClO}^2$  in 10 c.c. of liquid,



and corresponding with the formula  $C^2H^3ClO^2 + 164aq.$ , was found to remain unaltered for four months at ordinary temperature; but, when it was enclosed in a sealed tube, plunged into boiling water for various times, and then cooled as quickly as possible, it was found, by trituration with a standard solution of soda or baryta, to have undergone decomposition to the extent shown in the following table.

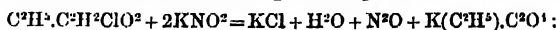
I. represents the number of hours the solution was heated; II. the percentage of  $C^2H^3ClO^2$  decomposed:—

I.	0	2	4	6	11	14	16	18	21	24	27	30
II.	0.0	6.0	11.0	14.5	23.0	28.0	31.5	35.0	38.0	42.5	45.0	51.5
I.	33	37	43	48	72	96	120	144	192	332	430	
II.	53.5	56.0	62.5	66.0	76.5	82.0	87.5	90.5	93.0	97.0	97.5	

(Buchanan, *Deut. Chem. Ges. Ber.* iv. 340).

*Phenyl chloracetate*,  $C^6H^5.C^2H^3ClO^2$ , is obtained by heating phenol with chloracetyl chloride; it forms silky glistening needles, melting at  $40.2^\circ$ , insoluble in water, soluble in alcohol and ether. Heated with alcoholic ammonia in a sealed tube, it is converted into phenyl amidacetate,  $C^6H^5.C^2H^3(NH^2)O^2$ , which crystallises in white needles, soluble in water, almost insoluble in alcohol and ether (E. W. Prevost, *J. pr. Chem.* [2] iv. 379).

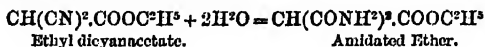
When an alcoholic solution of *ethyl chloracetate* is heated with potassium nitrite, potassium ethyloxalate is formed according to the equation:



(Steiner, *Deut. Chem. Ges. Ber.* v. 383).

**Dichloroacetic Acid**,  $C^2H^2Cl^2O^2$ .—When ethyl dichloroacetate is digested at a temperature below  $100^\circ$  with a solution of potassium cyanide in dilute alcohol till it no longer smells of hydrocyanic acid, the filtered liquid, after separation of the alcohol, shaken up with ether, and the ethereal solution evaporated, a substance is left which, after crystallisation from alcohol and water, is scentless and tasteless; melts at  $190^\circ$ – $191^\circ$ ; has a neutral reaction; is very soluble in ether, moderately soluble in alcohol; dissolves readily in hot, slightly in cold water, and crystallises from the solution in prisms. Its aqueous solution is decomposed by potash in the cold, with evolution of ammonia.

The crystalline compound has the composition  $C^4H^4N^2O^4$ , and may be regarded as an amidated ether,  $CH(CONH^2)^2.COOC^2H^3$ , derived from an unknown acid,  $CH(COOH)^2$ . It is probably formed by the action of water in presence of excess of acetic acid on ethyl dicyanacetate, produced in the first instance by the action of potassium cyanide on ethyl dichloroacetate in presence of alcohol:



The ether treated with potash yields oxalic, malonic, and glycollic acids, which are also found in the aqueous liquid separated from the ethereal solution of the amidated ether in the course of its preparation (Amato, *Gazzetta chimica italiana*, i. 690).

**Trichloroacetic Acid**,  $CCl^3.COOH$ . (De Clermont, *Compt. rend.* lxxiii. 112, 501; lxxiv. 942; Judson, *Zeitschr. f. Chem.* [2] vii. 40).—This acid is easily prepared by the action of nitric acid on chloral or its hydrate. When chloral hydrate is put into a flask with three times its weight of fuming nitric acid, and the mixture left to itself in the sun, a continuous disengagement of nitrogen tetroxide ensues, which ceases at the end of three or four days. On distilling the mixture, the temperature rises rapidly to  $123^\circ$ , at which point a mixture of nitric acid and water distils over; it then rises gradually to  $195^\circ$ , and the distillate consists of the last portion of the nitric acid, together with a small quantity of trichloroacetic acid; the temperature then remains steady at  $195^\circ$ , and the distillation proceeds regularly so long as any acid remains in the retort; the product is a colourless, transparent liquid, which crystallises at  $44.8^\circ$ . In one operation, 300 grams of trichloroacetic acid may be produced from 480 grams of chloral hydrate (De Clermont).

Trichloroacetic acid boils at  $195^\circ$  (Judson).

The trichloroacetates of *barium*, *strontium* and *calcium*, prepared by adding an excess of trichloroacetic acid to the corresponding carbonates, and evaporating at ordinary temperatures over lime, have a composition represented by the general formula  $M^2(C^2Cl^3O^2)^2 + 6H^2O$ . The *sodium salt*, similarly prepared, consists of  $NaC^2Cl^3O^2 + 3H^2O$  (De Clermont).

The *lead salt*,  $\text{Pb}(\text{C}^2\text{Cl}^3\text{O}^2)^2 + \text{H}^2\text{O}$ , crystallises in large rhombic prisms, easily soluble in water, less soluble in alcohol, and only sparingly in ether. The *copper salt*,  $\text{Cu}(\text{C}^2\text{Cl}^3\text{O}^2)^2 + 6\text{H}^2\text{O}$ , forms fine crystals, resembling copper sulphate. In preparing it an excess of copper carbonate must be avoided, or else the acid will be decomposed, with production of chloroform (Judson).

The following trichloroacetates have likewise been analysed by De Clermont:—

Acid potassium salt	$\text{KC}^2\text{Cl}^3\text{O}^2 \cdot \text{C}^2\text{Cl}^3\text{HO}^2$
Lithium salt	$\text{LiC}^2\text{Cl}^3\text{O}^2 \cdot 2\text{H}^2\text{O}$
Magnesium salt	$\text{Mg}(\text{C}^2\text{Cl}^3\text{O}^2)^2 \cdot 4\text{H}^2\text{O}$
Nickel salt	$\text{Ni}(\text{C}^2\text{Cl}^3\text{O}^2)^2 \cdot 4\text{H}^2\text{O}$

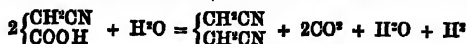
These salts crystallise from solutions of the respective carbonates in trichloroacetic acid. The magnesium and lithium salts require several months for crystallisation; the crystals of both are deliquescent, and those of the latter can be kept only in sealed tubes.

*Isobutyl Trichloroacetate*,  $\text{CH}^3\text{CH}(\text{CH}^3)^2 \cdot \text{C}^2\text{Cl}^3\text{O}^2$ , obtained by prolonged digestion of 2 mol. isobutyl alcohol, 2 mol. trichloroacetic acid, and 1 mol. sulphuric acid, distilling, washing with sodium carbonate and water, and drying over calcium chloride, is a colourless liquid of agreeable odour, heavier than water, boiling at  $187^\circ\text{--}189^\circ$  (Judson).

*Trichloroacetanilide*,  $\text{C}_6\text{H}_5 \cdot \text{C}^2\text{Cl}^3\text{O} \cdot \text{HN}$ , may be obtained by gradually mixing ethereal solutions of trichloroacetyl chloride and aniline; it is insoluble in cold water and dissolves very sparingly in boiling water, but easily in alcohol and ether; it crystallises in silvery scales which melt at  $82^\circ$ . *Trichloroacetobutidide*, prepared by an analogous process from toluidine, crystallises in fine six-sided prisms, which are often an inch long and melt at  $102^\circ$  (Judson).

When trichloroacetic acid is gradually added to a solution of *potassium sulphate*, sulphurous oxide is first given off, then carbon dioxide and chloroform. The solution, boiled till it ceases to smell of chloroform, contains, besides sulphate and hyposulphate of potassium, a very soluble salt,  $\text{CHCl}(\text{SO}^2\text{K})\text{CO}^2\text{K} + 12\text{aq}$ , which crystallises in beautiful perfect square-based octahedrons, with the basal pinacoids predominating, like the crystals of potassium ferrocyanide. These crystals remain unaltered in a vacuum over sulphuric acid, but lose water at  $100^\circ$ . The salt begins to decompose above  $165^\circ$ , and, when heated sufficiently, swells up, burns with a sulphur flame, and leaves a residue of potassium chloride and sulphate, discoloured by carbon. Its solution is not precipitated by baryta-water, neutral or basic lead acetate, or silver nitrate. This solution is not altered by boiling with potash, but suffers partial decomposition, when kept for some hours at  $140^\circ$ , and if heated to this temperature with potassium sulphate, it yields a considerable quantity of potassium chloride, so that the chlorine in the salt probably becomes replaced by hydrogen or by the group  $\text{SO}^2\text{K}$  (Rathke, *Ann. Ch. Pharm.* clxi. 149).

**Cyanoacetic Acid.** The electrolysis of this acid yields results analogous to those of acetic acid itself, the positive cell being found to contain a deliquescent acid substance, which is separable by means of ether, and agrees in physical and other characters with ethylene cyanide,  $\text{C}^2\text{H}^2\text{C}^2\text{N}^2$ , being solid at ordinary temperatures, melting at  $37\text{--}8^\circ$ , and being resolved by boiling with potash into ammonia and ethylene-succinic acid. The decomposition may be represented by the equation:



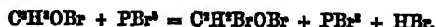
being exactly analogous to the electrolytic decomposition of acetic acid into carbon dioxide and dimethyl or ethane (G. E. Moore, *Silk. Am. J.* [3] iii. 177).

**Phenyl-acetic Acid.** See TOLUIC ACID.

**Thioacetic Acid**,  $\text{CH}^3 \cdot \text{COSH}$ , subjected to electrolysis, yields acetyl bisulphide  $(\text{C}^2\text{H}^2\text{O})^2 \text{S}^2$  (Bunge, *Deut. Chem. Ges. Ber.* iii. 576).

**Trimethyl-acetic Acid.** See VALERIO ACID.

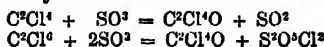
**ACETIC BROMIDE**, or **ACETYL BROMIDE**,  $\text{C}^2\text{H}^3\text{OBr}$ .—When this compound is heated for some hours in a tube to  $140^\circ\text{--}150^\circ$ , with an equivalent quantity of phosphorus pentabromide, bromoacetyl bromide,  $\text{C}^2\text{H}^2\text{BrOBr}$  is formed according to the equation:



The bromoacetyl bromide passes over on rectification between  $150^\circ\text{--}155^\circ$  (Samoadaky, *Zeitschr. f. Chem* [2] vi. 105).

**ACETIC CHLORIDE**, or **ACETYL CHLORIDE**,  $C^2H^3OCl$ , treated in like manner with phosphorus pentachloride, yields chloroacetyl chloride,  $C^2H^2ClOCl$  (Samoadsky).

*Trichloroacetyl Chloride*,  $C^2Cl^3O = C^2Cl^2OCl$ , is formed by heating di- or trichloride of carbon with sulphuric anhydride to  $150^\circ$ :



(Prudhomme, *Compt. rend.* lxx. 1137).

Respecting the conversion of acetic chloride into ethyl alcohol by sodium amalgam, see ETHYL ALCOHOL.

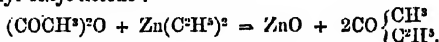
**ACETIC OXIDE** or **ANHYDRIDE**.  $(C^2H^3O)^2O$ . *Reaction with Stannic Acid*.

—When two parts of anhydrous acetic acid are heated with one part of stannic (or of metastannic) acid to  $150^\circ$  in a sealed tube, a syrupy liquid is obtained, crystallising on cooling in long needles which, after pressing between blotting-paper and drying over lime *in vacuo*, have the formula,  $SnO^2 \left[ \begin{smallmatrix} C^2H^3O \\ C^2H^3O \end{smallmatrix} \right] O$ .

Washed with anhydrous ether till the washings are free from acid, and dried *in vacuo*, this substance is converted into a body having the formula,  $SnO^2 \begin{pmatrix} C^2H^3O \\ C^2H^3O \end{pmatrix} O$ .

The first-named crystals, when exposed to air, become amorphous, and are finally transformed into a vitreous mass having the composition  $SnO^2 \begin{pmatrix} C^2H^3O \\ H \end{pmatrix} O$  (Lawrence, *Compt. rend.* lxxiv. 1524).

*Reaction with Zinc-ethyl*.—Acetic oxide treated with zinc ethyl in the nascent state yields methyl-ethyl ketone:



When a mixture of 2 mol. ethyl iodide and 1 mol. acetic oxide is added by drops to zinc-sodium in a cooled vessel, reaction sets in and is complete after 20 or 30 hours. On distilling and purifying the distillate in the usual way, by treatment with potash, combination with sodium bisulphite and decomposition of the resulting crystalline compound by distillation with an alkaline carbonate, methyl-ethyl ketone is obtained, boiling, after dehydration, between  $70^\circ$  and  $80^\circ$ . Other compounds boiling between  $100^\circ$  and  $210^\circ$ , are formed at the same time, probably resulting from the action of the zinc-ethyl on the methyl-ethyl ketone.

Zinc-ethyl, ready formed, acts with great violence on acetic oxide, evolving a large quantity of gas, which carries off with it a considerable portion of the liquid products.

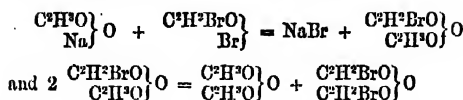
A mixture of methyl iodide and acetic oxide acts in like manner on zinc-sodium, yielding common acetone,  $(CH^3)^2CO$ , together with bodies boiling between  $70^\circ$  and  $190^\circ$  (Saytzeff, *Zeitschr. f. Chem.* [2] vii. 104).

Respecting the action of acetic oxide on carbohydrates, see CELLULOSE, GUM, SUGAR, STARCH, &c.

**Acetohypochlorous Oxide**,  $\begin{pmatrix} C^2H^3O \\ Cl \end{pmatrix} O$ , or **Chlorine Acetate**,  $CH^3.COOCli$ .

—When a slow stream of acetylene is passed into a solution of this compound in acetic oxide containing 8 to 10 grams of  $C^2H^3ClO^2$  to 35 to 40 grams of  $C^2H^3O^2$ , the gas is absorbed, with rise of temperature, acetic acid and methyl chloride are formed, and the acetylene either remains unaltered, or forms a compound not yet isolated. But if a very dilute solution of acetohypochlorous oxide be used (containing 15 parts  $Cl^2O$  to 100 parts acetic oxide), and cooled to at least  $-10^\circ$ , the acetylene is absorbed without perceptible formation of methyl chloride, and water throws down from the saturated solution a somewhat syrupy liquid, having a peculiar aromatic odour and boiling at  $120^\circ$  under a pressure of 2 centimeters. It has the composition  $C^2H^2 \begin{pmatrix} (C^2H^3O)^2 \\ (ClO)^2 \end{pmatrix}$  and may be regarded as the acetochlorhydrin of the tetratomic acetylene-alcohol  $C^2H^2(OH)^4$ . Aqueous potash, at the boiling heat, dissolves it quickly (Prudhomme, *Compt. rend.* lxx. 1137).

**Bromacetic Oxide**,  $C^2H^3Br^2O^2$ , or  $(C^2H^3BrO)^2O$ , the anhydride of monobromacetic acid, is formed by adding monobromacetic bromide,  $C^2H^3BrO.Br$ , to fused and finely powdered sodium acetate, and distilling. The distillate yields, by rectification, acetic oxide passing over between  $137^\circ$  and  $245^\circ$ , and bromacetic oxide at  $245^\circ$ . The reaction appears to take place by two stages, aceto-bromacetic oxide being first formed, and subsequently splitting up into acetic and dibromacetic oxides, thus:



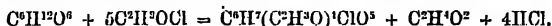
Bromacetic oxide does not solidify at  $0^\circ$ . When poured into water or exposed to moist air, it is gradually converted into monobromacetic acid. In alcohol it dissolves with formation of ethylic monobromacetate (II. Gal, *Compt. rend.* lxxi. 273, *Chem. Soc. J.* [2] ix. 23).

**ACETOBENZIDINE.** See BENZIDINE.

**ACETOBROMOPHENONE.** See ACETOPHENONE.

**ACETOCHLORAL.** Syn. with CHLORAL.

**ACETOCHLORHYDROSE,**  $\text{C}^4\text{H}^{10}\text{ClO}^3 = \text{C}^4\text{H}^7(\text{C}^2\text{H}^3\text{O})^2\text{ClO}^3$  (A. Colley, *Compt. rend.* lxx. 401).—A compound produced by the action of acetyl chloride on glucose. The action takes place at ordinary temperatures, but it is best to enclose the materials in sealed tubes cooled by a freezing mixture. With 5 mol. acetyl chloride to 1 mol. glucose, a colourless transparent mass is obtained. The reaction is:



On opening the tubes while immersed in the freezing mixture, hydrochloric acid escapes with violence; and on dissolving the residuo in chloroform, agitating with sodium carbonate, drying with calcium chloride, and evaporating off the chloroform, acetochlorhydrose remains as a semifluid, colourless, transparent, scentless, bitter mass, insoluble in water, easily soluble in alcohol, ether, and chloroform, slightly soluble in carbon bisulphide, nearly insoluble in benzene. It turns the plane of polarisation to the right:  $[\alpha] = 147^\circ$ . It was once obtained, under conditions not specified, as a perfectly dry crystalline mass, the analysis of which led to the formula above given, which is that of the acetochlorhydrin of glucose.

Acetochlorhydrose gives up the whole of its chlorine when treated in alcoholic solution with silver nitrate. Heated with sulphuric acid and alcohol, it gives off the odour of acetic ether. It does not reduce Fehling's solution. When heated with water in sealed tubes, it blackens and decomposes, but when treated in the same manner in shallow vessels exposed to the air, it remains colourless, and glucose is reproduced. It distils partially in a vacuum between  $150^\circ$  and  $240^\circ$ . The distilled product resembles the original substance, but has only half its rotatory power:  $[\alpha] = 71^\circ$ .

The reaction by which acetochlorhydrose is produced indicates that glucose is a pentatomic alcohol containing 5 hydroxyl-atoms. The sixth oxygen-atom probably binds together two atoms of carbon, as in diethylenic alcohol.

**ACETOCINNAMMONNE,**  $\text{C}^{10}\text{H}^{10}\text{O} = \text{CO} \begin{array}{l} \text{CH}^3 \\ \text{CH}-\text{CH} \end{array} - \text{C}^6\text{H}_5$ .—A ketone is

obtained, together with several other products, by the dry distillation of an intimate mixture of acetic oxide and cinnamic acids. It may be separated by repeated fractional distillation of that portion of the crude distillate which boils between  $220^\circ$  and  $270^\circ$ . When recently prepared it is a slightly yellow oily liquid of agreeable odour, turning darker when kept. Sp. gr. 1.008. Boiling point,  $240^\circ$ – $241^\circ$  (Engler & Leist, *Deut. Chem. Ges. Ber.* vi. 254).

**ACETODIBROMOXYLIDIDE.** See XYLIDINE.

**ACETONAPHTHYLAMIDE.** See NAPHTHYLAMIDE.

**ACETONE,**  $\text{C}^3\text{H}^4\text{O}$ .—The formation of this body by the action of zinc-sodium on a mixture of acetic oxide and zinc-methyl has already been mentioned (p. 11). It is also formed by oxidation of propylene with aqueous chromic acid (Berthelot, *Compt. rend.* lxxiii. 334), and, according to Schloosmich (*Zeitschr. f. Chem.* v. 336), when aldehyde vapour is passed over red-hot lime.

Acetone heated to  $100^\circ$ – $120^\circ$  for some days with liquid phosphene, yields a small quantity of liquid, which appears to be dichloracetone (T. Kempff, *J. pr. Chem.* [2] i. 402).

When acetone is treated with phosphorus pentasulphide, a violent reaction takes place, requiring, however, the heat of a water-bath to complete it; and two layers of liquid are obtained, the upper of which yields, by fractional distillation, duple-sulphacetone,  $\text{C}^6\text{H}^8\text{S}^2\text{O}$ , as a liquid boiling at  $183^\circ$ – $188^\circ$  (corr.), and having a vapour-density of 5.08 (calc. 5.45). It produces a burning sensation on the skin; gives off vapours which attack the eyes strongly; mixes with alcohol and ether, but not with water; gives a bulky white precipitate with mercuric chloride. The lower

liquid formed in the above reaction consists chiefly of ethereal compounds and a small quantity of duplo-sulphacetone (Wislicenus, *Zeitschr. f. Chem.* [2] v. 324).

**Compound of Acetone with Mercuric Oxide.**—When solution of mercuric chloride is slowly added to a mixture of acetone with dilute aqueous solution of potassium hydrate, the mercuric oxide first precipitated is dissolved, with production of a clear colourless liquid. This solution gelatinises when heated to ebullition, or on the addition of acid in slight excess. On dialysing the alkaline solution, the diffusate, at the end of two days, contains a large quantity of potassium chloride, some potassium hydrate, and but a very small amount of mercury. If the process of diffusion be continued, the diffusate being replaced by pure water twice each day, until it no longer affords a cloud when treated with solution of silver nitrate, the dialyser will contain a pure colloidal liquid, which, on careful evaporation to dryness, yields a resinoid residue having a composition represented by the formula  $2\text{CO}(\text{CH}_3)_2 \cdot 3\text{HgO}$ .

Water containing 2 p. c. of this compound retains its liquidity for months; a 5 p. c. solution remains liquid for some days, but produces a firm jelly on being heated to  $50^\circ$ . The liquid colloid hydrate is the *hydrosol* of the new compound; and the gelatinous hydrate, the *hydrogel* (v. 1088). The *alcosol* may be obtained by adding to a 1 p. c. hydrate an equal volume of alcohol, and evaporating the mixture over quicklime until most of the water is removed. This *alcosol*, on being submitted to prolonged ebullition, yields a jelly or *alcogel* corresponding to that produced on heating the hydrate—in the former case alcohol, and in the latter water, being associated with the mercuric ketone-compound. The hydrate, though neutral to test-paper, appears to be a weak acid, probably quadribasic.

Several ketones of the fatty series are capable of uniting with mercuric oxide in presence of alkali, to form compounds analogous to that obtained with acetone, but the hydrates or hydrosols of the mercuric compounds are very difficult to prepare, on account of the insolubility of the higher ketones in water (J. E. Reynolds, *Proc. Roy. Soc.* xix. 431).

**Bromacetone.**  $\text{C}^3\text{H}^5\text{BrO}$ .—Monobromacetone is readily formed by diluting acetone with 2–3 vols. of carbon sulphide, and adding a little less than the calculated quantity of bromine. After distilling off the carbon sulphide and excess of acetone, the product is left behind as a dark viscid mass. Freshly-precipitated silver oxide in presence of water converts it into a volatile liquid, having a sweet taste, and reducing alkaline solution of copper salts. This compound, which appears to be the alcohol of pyruvic acid, could not be obtained pure, as it seems to be decomposed by dehydrating bodies. Together with it, a smaller quantity of an acid,  $\text{C}^2\text{H}^3\text{O}^2$ , is formed, which in the free state forms a syrup having a sour and bitter taste, while the barium salt is a hard, amorphous mass (Emmerling, *Deut. Chem. Ges. Ber.* vi. 22).

**Chloracetones.**—Monochloracetone was first obtained by Riche, by the electrolysis of a mixture of acetone and hydrochloric acid. Borsche a. Fittig (*Ann. Ch. Pharm.* cxxviii. 111) denied the existence of this compound, because by passing chlorine into well-cooled acetone they obtained dichloracetone directly, without previous formation of the monochlorinated compound; they, therefore, regarded Riche's product as epichlorhydrin, which is isomeric with monochloracetone; this, however, was disproved by Linnemann (*ibid.* cxxiv. 170), who showed that the product in question, when reduced by nascent hydrogen, yields acetone. Kriwaxin (*Zeitschr. f. Chem.* [2] vii. 263), by heating acetone with chlorine, obtained no dichloracetone, but only monochloracetone and products of higher boiling point, apparently a mixture of acetone and monochloracetone. According to Glutz a. Fischer (*J. pr. Chem.* [2] iv. 52), the product obtained by the action of chlorine on perfectly dry acetone is a mixture of mono- and dichloracetone, the former predominating. C. Bischoff, in like manner, obtained a product which yielded by fractional distillation a liquid boiling at  $110^\circ$ – $125^\circ$  and containing 39 p.c. chlorine: a portion of this boiling at  $120^\circ$  contained 43 p.c. chlorine; now monochloracetone contains 38·4 p.c. and dichloracetone 53·6 p.c. chlorine: hence it appears that the product obtained consisted chiefly of monochloracetone. Lastly, E. Mulder (*Deut. Chem. Ges. Ber.* v. 1007) finds that either mono- or dichloracetone may be obtained at pleasure according to the proportion of chlorine used. To prepare monochloracetone he passes a small quantity of chlorine through acetone, washes the product with a little water, distils it over a mixture of calcium chloride and marble (the latter to saturate the free hydrochloric acid formed); subjects the liquid which passes over between  $100^\circ$  and  $140^\circ$  to fractional distillation, and thereby obtains a liquid which boils at about  $119^\circ$  and contains 39·3 p.c. carbon and 5·9 hydrogen, the formula  $\text{C}^3\text{H}^5\text{ClO}$  requiring 38·9 carbon and 5·4 hydrogen.

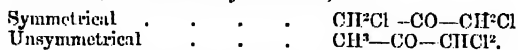
**Monochloracetone**,  $\text{CH}_3\text{—CO—CH}_2\text{Cl}$ , is also easily produced by the action of strong sulphuric acid on epichlorhydrin,  $\text{OH}^2\text{Cl—CCl—CH}_2^2$  (L. Henry, *Deut. Chem. Ges. Ber.* v. 966), and by the action of hypochlorous acid on acetone (Mulder),

Monochloroacetone, heated with potassium acetate and alcohol, is converted into the corresponding acetyl-compound, mono-acetyl-acetone,  $\text{CH}_3\text{—CO—CH}^2(\text{OC}^2\text{H}^3\text{O})$ , a limpid liquid boiling at  $175^\circ$  and having a refreshing smell and bitter taste. When recently prepared it is neutral, but in contact with moist air or water, in which it is readily soluble, it soon requires an acid reaction. The replacement of the acetyl in this compound by hydrogen would give the alcohol  $\text{CH}_3\text{—CO—CH}^2\text{OH}$ , corresponding with pyruvic acid; but this transformation has not yet been effected (Henry).

Monochloroacetone is converted by *fuming nitric acid* into a compound  $\text{C}^2\text{H}^4\text{Cl}(\text{NO}^2)\text{O}$ , which crystallises readily from water-alcohol and ether;—by *alcoholic ammonia* into sal-ammoniac and an oil having the odour of naphthylamine;—by *alcoholic potassium cyanide* into cyanacetone,  $\text{C}^2\text{H}^3(\text{CN})\text{O}$ ;—with the neutral sulphates of the alkali-metals it yields metallic chlorides and acetone-sulphonic acid (Glutz, *J. pr. Chem.* [2] i. 14).

The reactions of monochloroacetone with *hydrocyanic acid* will be described further on.

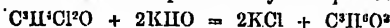
**Dichloroacetone**,  $\text{C}^2\text{H}^2\text{Cl}^2\text{O}$ .—Of this compound there are two modifications, one symmetrical in structure, the other unsymmetrical, viz.:



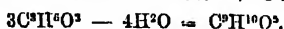
The symmetrical modification is obtained by oxidising dichlorhydrin,  $\text{CH}^2\text{Cl—CHOH—CH}^2\text{Cl}$ , with chromic acid mixture. It boils at  $170^\circ\text{—}171^\circ$ , forms well-crystallised compounds with acid sodium sulphite, potassium iodide, and potassium sulphocyanate; treated in ethereal solution with powdered potassium cyanide, it is converted into a compound having the composition  $\text{C}^2\text{H}^2\text{Cl}^2\text{NO}^2$  (Glutz a. Fischer, *J. pr. Chem.* [2] iv. 52; *Chem. Soc. J.* [2] ix. 922).

The unsymmetrical modification is obtained by passing chlorine into acetone till it is saturated, the liquid being heated in the water-bath towards the end of the operation (Fittig;—Glutz a. Fischer).—E. Mulder, (*Deut. Chem. Ges. Ber.* v. 1007), passes chlorine in excess into acetone at ordinary temperatures, washes the product with water, distils it over a mixture of chloride and carbonate of calcium, and, finally, by fractional distillation, obtains a product which boils at  $120^\circ$  and contains 55.5 p.c. chlorine, the formula  $\text{C}^2\text{H}^2\text{Cl}^2\text{O}$  requiring 55.9.

Dichloroacetone heated with *potassium hydrate* yields a glucose-like body,  $\text{C}^2\text{H}^2\text{O}^3$ , similar to that produced by the action of water on sulphacetate of lead, together with a brown substance, which forms with lead acetate the compound  $\text{Pb}(\text{C}^2\text{H}^2\text{O}^3)^2$ . The formation of these two bodies is represented by the equations:



and:



Similar products are obtained by the action of potassium sulphhydrate on dichloroacetone.

With solid potassium cyanide the unsymmetrical dichloroacetone yields a product isomeric with that which is obtained from the symmetrical modification (Mulder, *Deut. Chem. Ges. Ber.* v. 1007).

Dichloroacetone, heated with excess of water to  $200^\circ$  for six hours, yields a large quantity of lactic acid (Linnemann a. v. Zotta, *Ann. Ch. Pharm.* clix. 247).

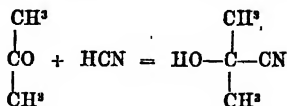
**Dichlorodibromacetone**,  $\text{C}^2\text{H}^2\text{Cl}^2\text{Br}^2\text{O}$ , is formed, together with the compound  $\text{C}^2\text{H}^2\text{BrCl}^2\text{O}$  (not obtained pure), by the action of bromine or dichlorhydrin. With water cooled nearly to  $0^\circ$  it forms, with considerable rise of temperature, a crystalline hydrate,  $\text{C}^2\text{H}^2\text{Cl}^2\text{Br}^2\text{O} + 4\text{H}^2\text{O}$ , which may be purified by pressure and recrystallisation from water and alcohol; from its alcoholic solution it is separated by water in dazzling white crystalline scales, or sometimes in larger crystals. It gives off its water of crystallisation when left over oil of vitriol, or when fused; in the latter case two layers of liquid are formed at  $49^\circ\text{—}50.5^\circ$ .

Anhydrous dichlorodibromacetone is a colourless heavy liquid, which does not solidify at  $10^\circ$ , gives off vapours which attack the eyes strongly, and is decomposed by distillation. By exposure to the air it is reconverted into the hydrate. It is decomposed by water, alcohol, and alkalis, with formation of similar products of decomposition. With alcohol at  $160^\circ$  the products are—besides chloride and bromide of ethyl—formic and glycolic acids, together with traces of carbonic acid, acetic acid, and an oily chlorinated body. With barium hydrate, formate and glycolate are obtained, together with larger quantities of carbonate and acetate. Oxalic acid is also formed, especially in strong solutions, together with an amorphous substance which interferes with the crystallisation of the glycolate. With hydriodic acid, dichlorodibromacetone appears to yield dichlorhydrin (Carius, *Deut. Chem. Ges. Ber.* iii. 393; *Zeitschr. f. Chem.* [2] vi. 533).

When dichlorodibromacetone is acted upon by zinc and dilute sulphuric acid, and heated from time to time to a temperature not exceeding 40°, a slow reaction is set up, which lasts for several weeks, the product consisting of acetone and a brominated compound (probably isopropyl bromide), not separable by distillation (Lange, *Deut. Chem. Ges. Ber.* vi. 98).

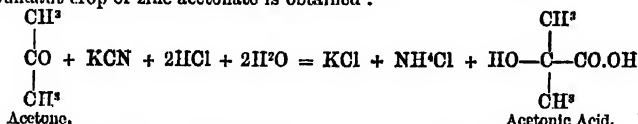
**Cyanogen-derivatives of Acetone.** (Urech, *Ann. Ch. Pharm.* clxiv. 255).

1. *Acetone-cyanhydrin*,  $C^3H^5NO = C^3H^4O.CNH$ .—This compound is formed by direct combination when dry hydrogen cyanide is passed into cooled acetone, and passes over for the most part at 120°, when the product, after remaining for some time, is distilled:

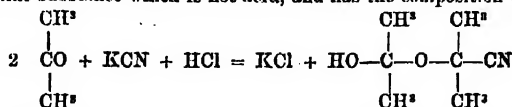


*Acetone-cyanhydrin* is a very unstable compound, the addition of silver nitrate giving rise to the formation of silver cyanide and the liberation of acetone. By allowing a portion of the acetone which had been saturated with hydrocyanic acid to remain for some months, heating it in a sealed tube to 100°, and allowing the more volatile portions to evaporate spontaneously, a yellow syrup was obtained which yielded ammonia and acetic acid,  $C^2H^4O^2$ , when boiled with a dilute mineral acid; when, however, the heating in a sealed tube was much prolonged, a brown mass was obtained which no longer yielded acetic acid. The action of alkalis on it gave rise to ammonia, together with a small quantity of a substance crystallising from water in efflorescent prisms.

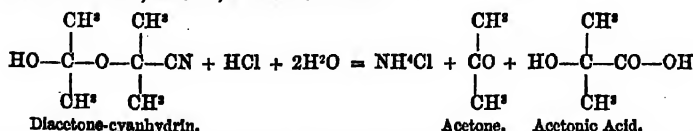
Acetic acid is more readily produced by the action of nascent hydrocyanic acid on acetone, as when slightly moist potassium is covered with acetone, and hydrochloric acid is added in excess in aqueous solution, or passed into the liquid in the state of gas. On exhausting the resulting brown mass with ether, evaporating the ethereal solution, dissolving the residue in water, and neutralising with zinc carbonate, an abundant crop of zinc acetate is obtained:



When, however, for each molecule of potassium cyanide present, only one molecule of hydrochloric acid is added, the ethereal solution of the product deposits on evaporation a crystalline substance which is not acid, and has the composition  $C^3H^5NO^2$ .



*Diacetone-cyanhydrin*, the product thus obtained, is easily soluble in water, alcohol, and ether, and crystallises from these solvents in thick shining anhydrous prisms. It melts between 135° and 162°, and sublimos below its melting point in long, colourless needles. It is decomposed at the ordinary temperature by hydrochloric acid into ammonium chloride, acetone, and acetic acid.



If the products of this reaction be distilled, a distillate is obtained consisting principally of acetone; and when this distillate is treated with quicklime to remove free acid and water, and the acetone separated by distillation, a residue is left containing a body which crystallises in prisms, and contains the elements of calcium chloride with two molecules of monacetonecyanhydrin,  $CaCl^2.2C^3H^5NO$ .

An attempt to form this substance by the addition of calcium chloride to the ethereal solution of the crude product obtained by the action of hydrochloric acid on acetone and potassium cyanide, led to the formation of a compound of diacetonecyanhydrin and calcium chloride,  $CaCl^2.C^3H^5NO^2 + 5H^2O$ , which separated from its

etheral solution in large crystals. When dried at  $100^{\circ}$  it contains  $\text{CaCl}_2 \cdot \text{C}^3\text{H}^3\text{NO}^3 + \text{H}^2\text{O}$ .

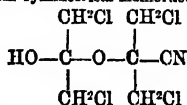
Acetone-cyanhydrin is regarded by Urech as analogous to Völkel's hydrocyanate of benzoyl hydride,  $\text{C}^7\text{H}^5\text{O} \cdot \text{CNH}$  (i. 570), and the splitting up of diacetone-cyanhydrin under the influence of hydrochloric acid is analogous to that of amygdalin when subjected to the action of the same reagent.

$\text{CH}^2\text{Cl}$   
 $\text{HO}-\text{C}-\text{CN}$ , is formed by gently heating monochlor-  
 $\text{CH}^3$

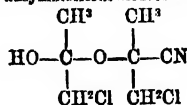
acetone with strong hydrocyanic acid and alcohol for 24 hours, and remains, on evaporation, as a thin oily liquid, which, when heated with hydrochloric acid, yields ammonium chloride and monochloroacetic acid,  $\text{Cl}(\text{CH}^2\text{Cl})(\text{CO} \cdot \text{OH})(\text{OH} \cdot \text{CH}^3)$ , crystallising in prisms, which have a pure sour taste (Bischoff).

*Tetrachloro-diacetone-cyanhydrin*,  $\text{C}^4\text{H}^2\text{Cl}^4\text{NO}^2$ .—Bodies having this composition are obtained by the action of potassium cyanide on the two modifications of dichloroacetone. The unsymmetrical dichloroacetone treated with aqueous potassium cyanide yields a compound crystallisable from water; the symmetrical dichloroacetone treated in the same manner yields only a brown tarry liquid, which quickly turns black; but an etheral solution of this dichloroacetone treated with pulverised potassium cyanide yields a body crystallisable from alcohol, and isomeric with that which is obtained from the unsymmetrical dichloroacetone. The two modifications of tetrachloro-diacetone-cyanhydrin thus obtained are represented by the following formula:—

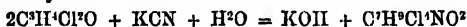
From symmetrical dichloroacetone.



From unsymmetrical dichloroacetone.

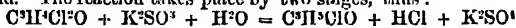


each being formed by the reaction:



(Glutz a. Fischer, *J. pr. Chem.* [2] iv. 52).

**ACETONE-SULPHONIC ACID**,  $\text{C}^3\text{H}^3\text{SO}^3 = \text{CO} \begin{Bmatrix} \text{CH}^3 \\ \text{CH}^2(\text{SO}^3\text{H}) \end{Bmatrix}$ . (Bender, *Zeitschr. f. Chem.* [2] vi. 162; *Deut. Chem. Ges. Ber.* iv. 517).—An acid produced by the action of alkaline sulphites on dichloroacetone. When 1 mol. dichloroacetone is mixed with a concentrated solution of 2 mol. neutral potassium sulphite, the liquid becomes hot, and the oily layer floating on the top quickly disappears. On evaporating to dryness over the water-bath, and treating the residue with boiling alcohol, potassium acetone-sulphonate,  $\text{C}^3\text{H}^3\text{KSO}^3$ , dissolves, while neutral potassium sulphate remains behind. The reaction takes place by two stages, thus:



and



The dichloroacetone used in this reaction was probably the unsymmetrical modification  $\text{CO} \begin{Bmatrix} \text{CH}^3 \\ \text{CHCl}^2 \end{Bmatrix}$ , since the symmetrical dichloroacetone  $\text{CO} \begin{Bmatrix} \text{CH}^2\text{Cl} \\ \text{CH}^2\text{Cl} \end{Bmatrix}$  would rather have yielded acetone-disulphonic acid.

The potassium salt separates from its alcoholic solution on cooling in white laminae, very soluble in water. Decomposed with an equivalent quantity of dilute sulphuric acid, it yields acetone-sulphonic acid, which may be extracted with alcohol and purified by neutralising it with lead carbonate and decomposing the resulting lead salt with hydrogen-sulphide: it then forms a colourless uncrystallisable syrup. The barium salt,  $(\text{CH}^3 \cdot \text{CO} \cdot \text{CH}^2\text{SO}^3)^2\text{Ba} + \text{aq.}$ , crystallises in colourless glistening scales, which give off part of their water over sulphuric acid, the whole at  $100^{\circ}$ . The cupric salt,  $3(\text{CH}^3 \cdot \text{CO} \cdot \text{CH}^2\text{SO}^3)^2\text{Cu} + \text{aq.}$ , forms blue-green scales, very soluble, and having an acid reaction. The lead salt,  $(\text{CH}^3 \cdot \text{CO} \cdot \text{CH}^2\text{SO}^3)^2\text{Pb} + \text{aq.}$ , crystallises in colourless scales, also very soluble, and having an acid reaction; it melts at  $140^{\circ}$  and decomposes completely at  $170^{\circ}$ .

When a dry mixture of potassium acetone-sulphonate and potassium cyanide is heated, a crystalline body sublimes, which is insoluble in alcohol and ether, but soluble in water. This body is a cyanide,  $\text{CH}^3-\text{CO}-\text{CH}^2-\text{CN}$ , which may be expected to yield an acid,  $\text{CH}^3-\text{CO}-\text{CH}^2-\text{COOH}$ , homologous with pyruvic acid.



**ACETONIC ACID**,  $C^3H^3O^2$ , or  $C \begin{Bmatrix} OH \\ (CH^3)^2 \\ COOH, \end{Bmatrix}$  is formed by the action of nascent hydrocyanic acid on acetone, by the spontaneous decomposition of acetone-cyanhydrin, and by the action of hydrochloric acid on diacetone-cyanhydrin (p. 15).

**Chloroacetic Acid**,  $C^2H^2ClO^2 = C \begin{Bmatrix} OH \\ CH^3 \\ CH^2Cl \\ COOH, \end{Bmatrix}$  is formed, together with sal-ammoniac,

when monochloroacetone-cyanhydrin is heated with hydrochloric acid (p. 16). It crystallises in prisms, which have a sour taste. Its *sodium salt*, obtained by saturation in the cold, is a deliquescent crystalline mass. The *ammonium salt* crystallises in prisms; the *lead salt*, obtained by dissolving recently precipitated lead carbonate in the aqueous acid, dries up in a vacuum to a vitreous mass soluble in water and in alcohol. The *ethylic ether* is an oily liquid, having a faint but agreeable odour, decomposed by distillation.

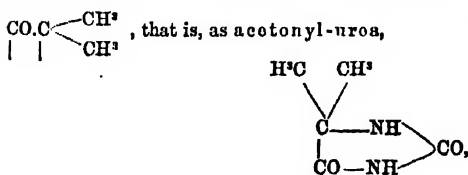
The chlorine in this acid may be replaced by cyanogen, yielding the nitril of an acid probably isomeric with oxyppyrotartaric acid (Bischoff, *Deut. Chem. Ges. Ber.* v. 866).

**ACETONINE**. The *oxalate* of this base is best prepared by treating the sulphocarbonate (1st Suppl. 29) with mercuric chloride (and then with sulphuretted hydrogen), whereby it is converted into the hydrochloride, and decomposing the latter with excess of silver oxalate or lead oxalate. On treating the product with boiling absolute alcohol, the acetone oxalate dissolves and separates from the solution as a beautiful silvery crystalline mass, having the previously determined composition  $C^3H^3N^2.C^2H^2O^4 + 2H^2O$ . It cannot be prepared by the action of oxalic acid on the sulphocarbonate, as the acetone is thereby completely decomposed (E. Mulder, *Zeitschr. f. Chem.* [2] v. 340).

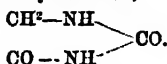
**ACETONITRIL**. See CYANIDES, ALCOHOLIC.

**ACETONYL-UREA**,  $C^3H^3N^2O^2$ . (Urech, *Ann. Ch. Pharm.* elxiv. 264).—When hydrochloric acid is added to commercial potassium cyanide (containing cyanate), covered with a layer of acetone, and the liquid, after the termination of the reaction, is poured off from the deposited crystals and evaporated, crystals of potassium chloride are left, mixed with long prisms, which, after recrystallisation from ether, and sublimation, have the composition  $C^3H^3N^2O^2$ .

This compound is formed by the conjunction of single molecules of acetone, hydrocyanic acid, and cyanic acid:  $C^3H^3O + HCN + HCNO = C^3H^3N^2O^2$ , and may be regarded as a urea having two hydrogen-atoms replaced by the acetonie acid residue



or as a dimethylated derivative of hydantoin,



Acetonyl-urea is easily soluble in water, alcohol, and ether, and separates from those solvents in large glistening prisms. It has a peculiar bitterish taste, and melts at  $175^\circ$ , at the same time subliming in long needles. With silver nitrate it forms the compound  $C^3H^3N^2O^2.AgNO^3$ , which crystallises in long prisms, easily soluble in water, and exploding when rapidly heated.

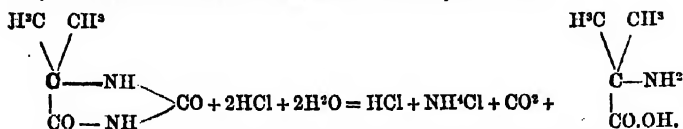
By warming a solution of acetonyl-urea with silver oxide, a white powder is produced, which, when purified by solution in ammonia and precipitation by acetic acid, has the composition of argento-acetonyl-urea,  $C^3H^3AgN^2O^2$ . When acetonyl-urea is boiled with baryta-water, the solution, after separation of the excess of baryta and acetonyl-urea, yields a barium salt having the composition  $(C^3H^3N^2O^2).Ba(OH)^2$ , or that of the barium salt of an acetoneuramic acid. The free acid is so unstable that when it is liberated by sulphuric acid, and the solution is agitated with ether, the ethereal solution yields acetonyl-urea on evaporation.

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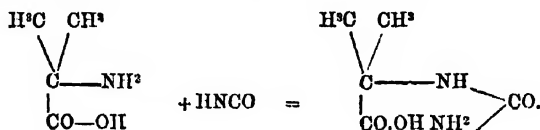
Acetonyl-urea, heated with hydrochloric acid to  $150^{\circ}$ – $160^{\circ}$ , splits up into carbonic anhydride, sal-ammoniac, and  $\alpha$ -amido-isobutyric acid—



The  $\alpha$ -amido-isobutyric acid thus obtained exhibits the characteristic properties of the glycocines. Its copper salt,  $\text{Cu}(\text{C}^{\circ}\text{H}^{\circ}\text{NO}^{\circ})_2$ , forms violet-blue crystals, easily soluble in water. The silver salt,  $\text{AgC}^{\circ}\text{H}^{\circ}\text{NO}^{\circ}$ , crystallises in silky needles soluble in water.

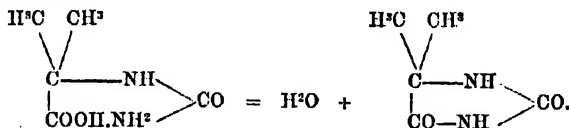
By evaporating to dryness the product of the action of hydrochloric acid on acetonyl-urea and exhausting the residue with spirit, a hydrochloride of  $\alpha$ -amido-isobutyric acid,  $\text{C}^{\circ}\text{H}^{\circ}\text{NO}^{\circ}\text{HCl} + \text{H}^{\circ}\text{O}$ , is obtained. It crystallises in short, colourless prisms, exhibits a strong acid reaction, is very soluble in water, moderately soluble in alcohol, and insoluble in ether. When its solution is evaporated with platinum chloride, crystalline masses are deposited corresponding with alanine platinochloride. When it is treated with solution of potassium nitrite, acetic acid is formed, nitrogen being set free at the same time.

*Synthesis of Acetonyl-urea from the Products of its Decomposition.*—When an aqueous solution of sulphate of alaphamidoisobutyric acid is evaporated with potassium cyanate, a residue is obtained, which, by exhaustion with alcohol, evaporation, and treatment with sulphuric acid, yields acetonyluramic acid, or  $\alpha$ -uramidoisobutyric acid.



This compound is moderately soluble in hot water and alcohol, but insoluble in ether. It melts and gives off water at  $160^{\circ}$ . Its silver salt,  $\text{C}^{\circ}\text{H}^{\circ}\text{AgN}^{\circ}\text{O}^{\circ}$ , forms tufts of needles slightly soluble in water.

Acetonyluramic acid, heated for a long time to  $130^{\circ}$ – $140^{\circ}$ , evolves water and yields acetonyl-urea:



**ACETOPHENONE.**  $\text{CO} \begin{Bmatrix} \text{C}^{\circ}\text{H}^{\circ} \\ \text{CH}^{\circ} \end{Bmatrix}$ . See PHENYL-METHYL KETONE.

**ACETOPIPERIDINE.** See PIPERIDINE.

**ACETOSACCHAROSE.** See SUGAR.

**ACETOTOLUIDE.**

**ACETOTOLUIDINE.** } See TOLUIDINE.

**ACETYL.** *Acetyl Chloride*,  $\text{C}^{\circ}\text{H}^{\circ}\text{OCl}$ , is one of the products of the action of chlorine on aldehyde (Wurtz, p. 35).

This compound is not decomposed, or but very slightly, by the action of heat alone; on heating it in sealed tubes for a long time to nearly  $30^{\circ}$  it gave only a trace of hydrochloric acid and a brown substance (Berthelot, *Bull. Soc. Chim.* [2] xvii. 391).

Acetyl chloride heated for several hours with excess of phosphorus pentachloride, is converted into carbon trichloride or hexachlorethane,  $\text{C}^{\circ}\text{Cl}^{\circ}$  (Hübner a. Müller, *Zeitschr. f. Chem.* vi. 328).

*Bromacetyl bromide*,  $\text{C}^{\circ}\text{H}^{\circ}\text{BrO.Br}$ , treated with zinc-methyl, yields an alcohol—probably  $\text{C}^{\circ}\text{H}^{\circ}\text{O}$ —which boils at  $110^{\circ}$ – $112^{\circ}$ , and when oxidised with chromic acid mixture, forms acetic acid and a small quantity of acetone (Shdanow, *Deut. Chem. Ges. Ber.* vi. 479). With zinc-ethyl, the same compound yields a decyl alcohol, boiling at  $155^{\circ}$ – $157^{\circ}$  (Anitow, *ibid.*).

**Trichloroacetyl compounds.**—The chloride  $C^2Cl^4O.Cl$  is easily obtained by the action of phosphorus trichloride on trichloroacetic acid; after rectification it boils regularly at  $118^\circ$ . Phosphorus pentachloride acts in a similar manner, but with formation of oxychloride, which is difficult to separate: hence it is better to use the trichloride. Trichloroacetyl chloride is converted by water into trichloroacetic and hydrochloric acids; by alcohol into ethyl trichloroacetate.

**Trichloroacetyl bromide**,  $C^2Cl^3O.Br$ , is obtained in like manner by the action of phosphorus tribromide on trichloroacetic acid, as a liquid boiling at about  $143^\circ$ ; its reactions are similar to those of the chloride.

**Trichloroacetyl iodide** is more difficult to prepare. Trichloroacetic acid treated with phosphorus tri-iodide yields a small quantity of a liquid boiling at about  $180^\circ$ , and decomposed by water and by alcohol; but its composition has not been satisfactorily made out (H. Gal, *Compt. rend.* lxxvi. 1019).

**ACETYLENE.**  $C^2H^2$ .—This hydrocarbon is formed by heating isethionic acid with potassium hydrate:



(Berthelot, *Compt. rend.* lxxix. 563).

Acetylene is readily oxidised by aqueous chromic acid, yielding acetic acid if the solution is dilute, formic acid and carbonic acid if it is concentrated (Berthelot). See ACETIC ACID (p. 4).

Acetylene passed together with *phosgene-gas* through a red-hot tube, is partly polymerised to benzene, &c., but does not yield any chlorinated organic compound (Berthelot, *Bull. Soc. Chim.* [2] xiii. 9).

On the reaction of acetylene with *aceto-hypochlorous oxide*, see page 11.

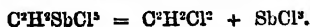
On the constitution of acetylene, see Carstanjon (*J. pr. Chem.* [2] iv. 419; *Chem. Soc. J.* [2] x. 231).

**Bromacetylene**,  $C^2HBr$ , is given off abundantly when dibromethylene,  $C^2H^2Br^2$ , is heated with alcoholic potash in an open vessel; but if the reaction takes place in a sealed tube, the bromine alone is abstracted and acetylene is produced (Fontaine, *Compt. rend.* lxx. 1361). Bromacetylene is likewise evolved when monobromethylene bromide,  $C^2H^2Br.Br^2$ , is added by drops to solid sodium ethylate (Alexejeff, *Zeitschr. f. Chem.* vi. 644).

Bromacetylene takes fire at ordinary temperatures in contact with the air, but if it be mixed with a considerable quantity of any indifferent gas, it merely becomes strongly heated on coming in contact with air, and forms white vapours of bromoacetic acid:  $C^2HBr + H^2O + O = C^2H^2BrO^2$ . This slow oxidation is favoured by sunshine, and does not take place in the dark; it is accompanied by a very perceptible odour of ozone (Fontaine, *Compt. rend.* lxx. 1361). Bromoacetic acid is also formed when an alcoholic solution of bromacetylene is exposed to the air (Glückner, *Ann. Ch. Pharm. Suppl.* vii. 197).

**Dibromobromide of Acetylene**,  $C^2H^2.2HBr$ , is formed by the prolonged action of hydrobromic acid on acetylene. It has the same boiling point as the isomeric hydrobromide of bromethylene,  $C^2H^2Br.BrHBr$  (Reboul, *Compt. rend.* lxxiv. 941).

**CHLORIDES OF ACETYLENE** (Berthelot a. Jungfleisch, *Ann. Ch. Phys.* [4] xxvi. 472). When dry acetylene is passed into antimony pentachloride, it is absorbed with considerable evolution of heat. If care has been taken to prevent the temperature from rising too high, the saturated liquid deposits, on cooling, magnificent plates consisting of a compound of acetylene and antimony perchloride,  $C^2H^2SbCl^5$ . This compound is immediately decomposed by water, and when it is heated by itself, an action takes place, resulting in the formation of antimony trichloride and *acetylene dichloride*:



If, however, a solution of the crystals in antimony pentachloride be heated, a more violent action takes place, giving rise to the formation of antimony trichloride and *acetylene tetrachloride*:



In practice both chlorides are produced at the same time, by heating the crude compound  $C^2H^2SbCl^5$  mixed with a certain proportion of antimony pentachloride, distilling, washing with water, and separating the chlorides by fractionation.

**Acetylene dichloride**,  $C^2H^2Cl^2$ , is a colourless limpid liquid, having an odour like that of chloroform, and boiling at about  $55^\circ$ . Water acts slowly on it at  $180^\circ$ , with formation of hydrochloric acid and condensed products. With potassium hydrate it forms acetic acid, and when heated to  $360^\circ$  in a sealed tube, it is entirely resolved into carbon and hydrochloric acid.

*Acetylene tetrachloride*,  $C^2H^2Cl^4$ , is a colourless liquid, smelling and tasting like chloroform, and boiling at about  $147^\circ$ . Water at  $180^\circ$  slowly decomposes it, with formation of hydrochloric acid. Chlorine converts it into carbon trichloride. Alcoholic potash converts it into glycollic acid:  $C^2H^2Cl^4 + 3H^2O = 4HCl + C^2H^2O^2$ ; but if the action be carefully regulated, the potash simply removes a molecule of  $HCl$ , leaving *chloracetylene dichloride*,  $C^2HCl_2Cl^2$ , a colourless liquid boiling at  $88^\circ$ . This last reaction also takes place when the tetrachloride is merely heated in a sealed tube to  $300^\circ$  for fifteen hours; and if the action be prolonged and the temperature raised to  $360^\circ$ , another molecule of  $HCl$  is removed; the product actually obtained consists, however, not of the residual dichloroacetylene  $C^2Cl^2$ , but of its polymeride, *Julin's carbon chloride*, or *hexachlorobenzene*,  $C^6Cl^6$ ; three molecules of acetylene tetrachloride taking part in the reaction:  $3C^2H^2Cl^4 = 6HCl + C^6Cl^6$ . This corresponds with the formation of benzene by polymerisation of acetylene, and explains the frequent formula of *Julin's chloride* in the destructive distillation of chlorinated organic compounds.

**ACHILLEA.** The Iva plant (*Achillea moschata*) has been chemically examined by A. v. Planta-Reichenau (*Ann. Ch. Pharm.* clv. 145).

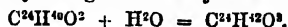
*Iva oil*.—The herb separated from the root yields, by distillation with steam, a bluish-green volatile oil, having a peculiar, not unpleasant odour, and tasting like peppermint-oil. On distillation it begins to boil at  $170^\circ$ ; the greater part passes over between  $180^\circ$  and  $210^\circ$ ; a very small quantity of yellow liquid between  $210^\circ$  and  $230^\circ$ ; a brown distillate, smelling like wormwood, between  $230^\circ$  and  $260^\circ$ ; and there remains a dark brown viscid, no longer bitter residue, which decomposes when heated above  $200^\circ$ , is not soluble in absolute alcohol, even when heated, but dissolves partially in ether and in turpentine-oil, leaving a carbonaceous residue.

*Ivaol*,  $C^{12}H^{20}O$ , or  $C^{24}H^{40}O^2$ .—This name is given to the portion of the distillate which passes over between  $170^\circ$  and  $210^\circ$ . It is a clear, faintly-yellowish liquid, having an extremely fragrant, strongly ethereal odour, which is very persistent, and perceptible a long way off. The liquid has a bitter, heating taste like that of peppermint-oil. Very small quantities dissolved in alcohol impart to that liquid the same powerful odour and agreeably bitter taste.

The fraction of the original oil which distills between  $230^\circ$  and  $260^\circ$  has nearly the composition of *ivaol*. The resin has the composition  $C^{14}H^{26}O$ .

*Ivain*,  $C^{24}H^{40}O^3$ .—This is a bitter substance contained in the alcoholic extract of the plant previously exhausted with water, together with stearic acid, which separates on cooling from the residue left after distilling off the alcohol. To prepare *ivain*, the dark green filtered liquid is warmed in the water-bath, with excess of alcoholic solution of neutral lead acetate; the resulting precipitate is separated by filtration; the somewhat concentrated filtrate is freed from lead by sulphuretted hydrogen, and from alcohol by evaporation over the water-bath; the residue is repeatedly treated with acetic acid (which extracts the nitrogenous principles to be hereafter mentioned) till the decanted acid remains colourless; then repeatedly washed with water till this liquid also runs from the tap-funnel colourless and no longer bitter, and the oily unctuous mass, which at first was heavier than water, floats on the top of it; this mass is repeatedly treated with absolute alcohol, and evaporated till the acetic acid is completely removed; and the alcoholic solution is finally treated with animal charcoal.

*Ivain* is a somewhat dark-coloured mass of the consistence of turpentine, which does not solidify at  $17^\circ$ , dissolves in alcohol, but not in water; the alcoholic solution is extremely bitter. Its composition, determined by analysis, is  $C^8H^{14}O$ ; if this formula be tripled, the compound may be regarded as a hydrate of *ivaol*:



*Nitrogenous principles of Iva*.—The aqueous extract of the plant contains two nitrogenous bodies, *achillein* and *moschatin*. To prepare them, the aqueous extract is repeatedly treated with absolute alcohol, as long as that liquid becomes coloured and acquires a bitter taste. The great bulk of the aqueous extract consists of a gummy light brown mass, which is insoluble in absolute alcohol, and becomes more pulverulent the more it is freed from *achillein* and *moschatin*. The brown alcoholic solution is completely freed from alcohol by distillation, and distilled water is added to the residue in successive portions and with frequent agitation. The liquid becomes turbid from separation of *moschatin*, which at first redissolves in the aqueous solution of *achillein*, but, on further addition of water, separates in flocks, which must be washed with water. The filtrate contains the *achillein*, also a little *moschatin*, and several acids not yet investigated; these may be removed by digestion for several days in the cold with successive portions of lead-hydrate. The filtrate, freed from lead by sulphuretted hydrogen, is evaporated in the water-bath in small portions, and with brisk stirring; the residue is dissolved in absolute alcohol, to remove traces

of a gummy substance; the solution again evaporated; and the residue redissolved in water to separate the moschatin. The residue obtained after another evaporation is regarded as pure achillein, if samples of the brittle mass dissolve completely in absolute alcohol and in water.

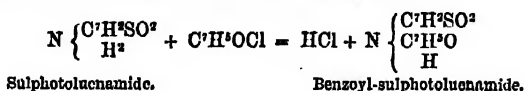
*Achillein* is a brittle, glassy, brown-red substance, which melts without decomposition at  $100^{\circ}$ , absorbs moisture very quickly from the air, dissolves readily, with wine-yellow colour, in water, less easily in absolute alcohol, and is insoluble in ether; it has an alkaline reaction, a peculiar odour, and a strongly bitter but not unpleasant taste. When dried at  $100^{\circ}$  it has the composition  $C^{22}H^{28}N^2O^{12}$ . It appears to be identical with the achillein obtained from *Achillea millefolium* by Zanon (i. 36), who, however, did not obtain it pure, and gave no analysis of it. When boiled continuously with strong potash-solution it gives off alkaline vapours having a peculiar odour. Chlorine-water decolorises achillein; lannic acid and ferrous sulphate have no action upon it. Ammonia dissolves it, and the solution, if exposed to the air till it no longer smells of ammonia, deposits a flocculent mass less soluble than achillein itself. Achillein is not precipitated by neutral or by basic acetate of lead. When boiled for several days with dilute sulphuric acid, or even with the acids which accompany it in the plant, it yields achilletin,  $C^{11}H^{12}NO^4$ , which separates as a dark brown powder; also sugar; a volatile product having a powerful aromatic odour; and apparently also ammonia. Achilletin is insoluble in water, very slightly soluble in alcohol; the alcoholic solution has an aromatic odour, but does not taste bitter.

*Moschatin*, obtained as above, may be purified by dissolving it in absolute alcohol, evaporating to dryness in the water-bath, warming the residue with water, and finally washing it with cold water till the mass can be pulverised under water. It then has the composition  $C^{24}H^{26}NO^7$ . It melts under water at the heat of the water-bath, and separates again in the pulverulent form on cooling; dissolves more easily in liquids containing achillein. It is somewhat more soluble in absolute alcohol than achillein, and has a more aromatically bitter taste.

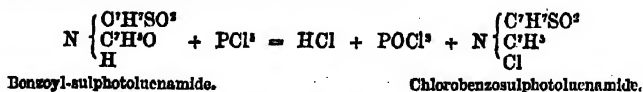
The ash of the Iva plant contains, as constituents soluble in water: alkaline carbonates and chlorides, small quantities of sulphuric acid and lime, and traces of magnesia. The portion insoluble in water, but soluble in nitric acid, contains large quantities of carbonic acid and lime, together with phosphoric acid and a little magnesia. The insoluble residue consists of silica and charcoals.

**ACIAMIDES.** (Anna Wolkow. *Zeitschr. f. Chem.* [2] vi. 577; vii. 422; *Deut. Chem. Ges. Ber.* v. 139; *Chem. Soc. J.* [2] x. 147, 413).—This term is applied to certain bodies which, though formed on the ammonia type, yet possess acid characters, such as the products obtained by the action of benzoyl chloride on sulphotoluenamide, sulphoxylonamide, sulphocymenamide, and sulphonaphthalenamide.

The amides,  $N(C^6H^4SO^2)H^2$ , produced by the action of ammonia on para- and meta-toluenesulphonic acids, are not decomposed by boiling potash-ley like amides in general, but yield crystalline compounds in which one hydrogen-atom of the amide is replaced by potassium. These metallic derivatives are extremely unstable, being decomposed even by carbonic acid, like the metallic derivatives of the alcohols and phenols, their ammoniacal hydrogen not having acquired acid characters under the influence of the acid radicle  $C^6H^4SO^2$ . But by treating these amides with the chloride of an acid radicle, such as benzoyl chloride, products are obtained having an acid reaction, and dissolving in ammonia, also in alkaline carbonates, with evolution of carbonic anhydride. Their formation may be illustrated by the following example:—



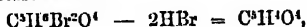
By the action of phosphorus pentachloride, these amides are transformed into chlorinated amides by substitution of Cl for OH, *e. g.*:—



For descriptions of the individual compounds, see Sulphotoluenamide, &c.

**ACIDS.** On the thermal effects of the combination of acids with bases, see **HEAT.**

**ACONIC ACID**,  $C^3H^4O^4$ .—This acid, originally obtained by Kekulé, by the action of alkalis on dibromopyrotartaric acid:

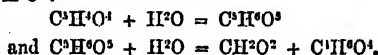


has been further examined by F. Moilly (*Deut. Chem. Ges. Ber.* vi. 242). It is very soluble in water, ether, and alcohol, and crystallises from the alcoholic solution in foliate groups of shining needles, melting at  $151^\circ$ .

From the mode of formation of aconic acid, it might be expected to be bibasic; but the constitution of its salts,  $M^+C^3H^3O^4$  and  $M^+(C^3H^3O^4)^2$ , shows that it is really monobasic, like its homologue, muconic acid; and this conclusion is confirmed by direct titration of the acid with caustic soda.

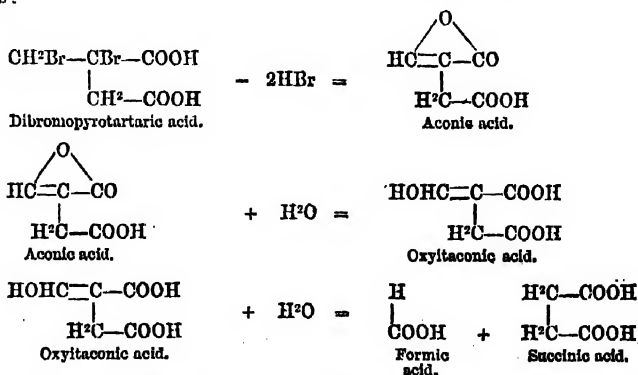
The aconates are easily prepared by digesting the corresponding carbonates with aqueous aconic acid. They mostly crystallise well, and dissolve very easily in water, excepting the silver salt, which is but sparingly soluble; a solution of sodium aconate is not precipitated by the salts of the earth-metals, or heavy metals. The *sodium salt*,  $NaC^3H^3O^4 + 3aq.$ , forms shining plates, or, by slow evaporation, well-defined crystals, which effloresce over oil of vitriol. The *silver salt*,  $Ag C^3H^3O^4$ , crystallises on cooling from a hot solution in small shining laminae. The *barium salt*,  $Ba(C^3H^3O^4)^2$ , is very soluble in water, is precipitated from the aqueous solution by alcohol, and crystallises from hot alcohol in slender needles. It shrinks together strongly in drying, and gives off about  $2\frac{1}{2}$  mol. water at  $150^\circ$ . The *copper salt*,  $Cu(C^3H^3O^4)^2 + 4aq.$ , crystallises in shining blue prisms, which give off their water with difficulty, acquiring at the same time a dirty green colour. The *zinc salt*,  $Zn(C^3H^3O^4)^2 + 8aq.$ , crystallises in large measurable crystals with strongly shining faces, melts below  $100^\circ$  in its water of crystallisation, and then swells up strongly in drying. *Methyl aconate*,  $CH^3.C^3H^3O^4$ , is formed by treating the silver salt with methyl iodide, the action, which begins in the cold, being completed by heating the mixture to  $100^\circ$  in a sealed tube. The resulting methyl aconate is dissolved out by ether, and crystallises from the residue of the ethereal solution in long needles melting at  $85^\circ$ , easily soluble in ether, moderately in alcohol, sparingly in water.

Aconic acid boiled for some hours with baryta-water is resolved into formic and succinic acids, with intermediate formation of a body having the composition of oxytaconic acid,  $C^3H^4O^5$ :



This decomposition of aconic acid is similar to that of its homologue, muconic acid, under the same circumstances; the latter, when boiled with baryta-water, being converted into succinic and acetic acids.

The formation of aconic acid from dibromo-pyrotartaric acid, its monobasicity, and its decomposition under the influence of baryta-water may perhaps be represented as follows:



The constitutional formula here assigned to aconic acid represents it, on the one hand, as a monobasic acid; on the other, as an anhydrido analogous to lactide. A similar constitution has been assigned by Dolbrück to muconic acid (*q.v.*)

**ACONITE ALKALOIDS.**—1. *Aconitine*.—This name appears to have been hitherto applied to several substances differing in their physical properties and physiological action. Schrott (*Schweiz. Pharm. Wochenschrift*, 1865, 205 and 213) dis-

tinguished an acrid and a narcotic principle in aconites, the former existing, with little or none of the latter, in the *Aconitum ferox* of Nepal, whereas all the European aconites contain more or less of the narcotic principle, the acrid principle being, however, greatly predominant in *Aconitum Napellus*. The narcotic principle of aconite has been shown by T. and H. Smith to be identical with narcotine (formerly called *Aconelline* (see 1st Suppl. p. 54). But even the acrid alkaloid, the aconitine, does not appear to be always the same when obtained from different sources. According to Schreiff, from 8 to 10 milligrams of English aconitine (said to have been prepared by Morson from *Aconitum ferox*) killed a rabbit in six minutes, whereas 400 milligrams of a German aconitine had previously been given to the same rabbit without killing it, and with production of different morbid symptoms.

According to Hübschmann (*Arch. Pharm.* cxxxv. 266), Swiss aconitine (prepared by Geiger's process, in the same way as atropine from belladonna root, i. 474) is a white amorphous, somewhat coarse-grained powder, which does not adhere to paper, and has a strongly bitter, but scarcely burning taste. It becomes soft and plastic in boiling water, and hardens to a brittle substance on cooling; dissolves in 2 parts of ether, 2·6 of chloroform, and 4·25 of alcohol, these solvents leaving it on evaporation as an amorphous mass having a vitreous lustre. Cold benzene unites it into resinous drops and slowly dissolves it; on heating the liquid, it dissolves quickly, and does not separate on cooling. English aconitine, on the other hand, is a fine dirty white powder, which adheres very strongly to paper, and has a burning, but not bitter taste. When immersed in boiling water, it remains pulverulent and does not melt. It requires for solution more than 109 parts of boiling ether, which, moreover, leaves a brown substance undissolved: the solution deposits small white crystals. One part of this aconitine dissolves in 230 parts of chloroform and 20 parts of boiling alcohol, from which solution it likewise crystallises. Cold benzene colours it dark and leaves it in the state of powder; on heating the liquid, the aconitine dissolves and separates on cooling, partly in crystals, partly in the state of powder.

The term 'crystallised aconitine' is applied by Duquesnel (*Compt. rend.* lxxiii. 207) to the active principle of *Aconitum Napellus*, prepared as follows:—

Selected roots are pulverised and mixed with  $\frac{1}{100}$ th part of tartaric acid, and the whole is exhausted with strong alcohol; the extract obtained is distilled out of contact with air, and at a temperature not exceeding 60°; and the residue is taken up with water to separate fatty and resinous bodies. The aqueous solution of impure aconitine tartrate thus obtained is treated with ether to remove colouring matters, precipitated by an alkaline bicarbonate, and again treated with ether, which dissolves the alkaloid; from this solution the base is obtained in crystals by evaporation, after addition of light petroleum oil, the crystals being colourless, rhombic or hexagonal tables.

Neither the alkaloid nor its salts with mineral acids are affected by a temperature of 100° or lower, either in the dry state or in contact with water; but at 100°, in contact with air and its own peculiar extractive liquor, it partly or wholly disappears. It is almost insoluble in water, but readily soluble in dilute acids, even in carbonic acid solution; it is not volatile at 100°, but at 130° it begins to decompose, and, apparently, to volatilise. It is soluble in ether, alcohol, benzene, and especially in chloroform; insoluble in glycerin and petroleum oils, both light and heavy. It rotates the plane of polarisation to the left, and is amorphous when obtained by precipitation of its salts by alkalis; in this condition it contains water of hydration, which is lost at 100°, without change of appearance; it has a feeble alkaline reaction.

Duquesnel finds in aconitine, prepared as above, 60·21 p.c. carbon, 7·44 hydrogen, 2·61 nitrogen, and 29·74 oxygen; whence he deduces the improbable formula  $C^{22}H^{14}NO^{10}$ .\* He regards it as a glucoside, and considers that this view explains the spontaneous deterioration of various pharmaceutical preparations of aconite on keeping.

From experiments by Gréhaud and Duquesnel (*Compt. rend.* lxxiii. 209; *Chem. Soc. J.* [2] ix. 948), it appears that small doses of aconitine subcutaneously injected are analogous in their physiological effects to curarine, destroying the motor power of nerves.

**2. Napelline.**—This is an alkaloid obtained by Hübschmann (*N. Repert, Pharm.* vi. 421) from crude aconitine. The crude base is treated with the smallest quantity of ether that will suffice to dissolve out the aconitine; the filtered solution is precipitated with neutral lead acetate; excess of lead is thrown down by hydrogen sulphide; and the filtrate is evaporated to dryness with addition of potassium carbonate. The residue is then exhausted with absolute alcohol, and the alcoholic solution is decolorised with animal charcoal and evaporated to dryness.\* Napelline thus obtained is a white electric powder, having a bitter, afterwards burning taste, and an alkaline

\* According to v. Planta's analysis, aconitine contains 67·97 C., 8·79 H., 3·42 N. and 19·82 O., leading to the generally received formula  $C^{22}H^{14}NO^{10}$  (i. 55).

reaction. It evolves nitrogenous vapours when burnt; neutralises acids completely; dissolves in water more easily than aconitine; and is therefore not precipitated from dilute solution by ammonia. It also dissolves more easily than aconitine in weak spirit, but less easily in ether.

3. *Acolyctine* and *Lycocotonine*.—These alkaloids, first obtained by Hübschmann from the root of wolfsbane (*Aconitum Lycocotum*, 1st Suppl. 55, 793), have been further examined by Schrott (*N. Report. Pharm.* xx. 611, 705), whose description of acolyctine agrees with that given by Hübschmann. Lycocotonine crystallises, according to Schrott, in white prisms and needles, having an intensely bitter taste, soluble in alcohol, chloroform, ether, benzene, amyl alcohol, petroleum spirit, oil of almonds, and oil of turpentine; only sparingly soluble in water (1 part in 800 at 17°); its aqueous solution gives, with bromine-water, a yellow precipitate of microscopic needles, and with potassium-mercuric iodide, a thick precipitate becoming crystalline on standing.

From a large number of physiological experiments made on men, rabbits, and frogs, it appears that the action of acolyctine and of lycocotonine is analogous to that of aconitine, and about one-third as energetic as that of napelline.

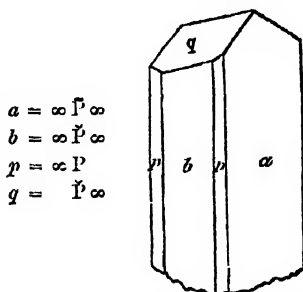
On the Alkaloids of Aconite, see also Flückiger, *Arch. Pharm.* [2] cxli. 196; *Jahresb.* 1870, 836.

#### ACORUS OIL. See OILS, VOLATILE.

**ACRIDINE**,  $C^{12}H^9N$  (Gräbe & Caro, *Ann. Ch. Pharm.* clviii. 265).—A basic substance obtained from crude anthracene. When the semi-solid portion of coal-naphtha, which boils between 300° and 360°, is treated with dilute sulphuric acid, and the acid solution is precipitated with potassium dichromate, a dirty brown precipitate is obtained which dissolves on repeated treatment with boiling water; and the resulting solution, after filtration and cooling, yields orange-yellow crystals of acridine chromate. These, when freed from mother-liquor by washing, and heated with ammonia, yield the free base, which may be purified by converting it into hydrochloride, recrystallising, and again precipitating with ammonia.

Acridine crystallises in small, brownish-yellow, transparent, four-sided rectangular prisms of the rhombic system, often having their edges only narrowly truncated by the vertical prisms  $\infty P$ , and terminated by obtuse domes. This combination (fig. 1) is represented by the formula  $\infty P \infty, \infty \bar{P} \infty, P \infty, \infty P$ .

Fig. 1.



$$\begin{aligned} a &= \infty \bar{P} \infty \\ b &= \infty \bar{P} \infty \\ p &= \infty P \\ q &= \bar{P} \infty \end{aligned}$$

$$\text{Axes } a : b : c = 0.6556 : 1 : 0.3316.$$

Angles.	Calc.	Obs.
$\infty P : \infty P$	$= 113^{\circ}30'$	
$\infty P : \infty \bar{P} \infty$	$=$	$123^{\circ}15'$
$\bar{P} \infty : \bar{P} \infty$	$= 143^{\circ}0'$	$143^{\circ}5'$
$\bar{P} \infty : \infty \bar{P} \infty$	$=$	$108^{\circ}30'$

Acridine melts at 107°, distils without alteration at a temperature above 360°, and sublimes even below its melting point in large broad needles. Its vapour-density is by experiment 6.10, agreeing nearly with that required by the formula  $C^{12}H^9N$ :  $\frac{12 \cdot 12 + 9 \cdot 1 + 14}{2} \times 0.0693 = 5.85$  (Gräbe, *Deut. Chem. Ges. Ber.* v. 15). It is

almost insoluble in cold, and but slightly soluble in boiling water; but dissolves readily in alcohol, ether, carbon bisulphide, and hydrocarbons. The dilute solutions show a beautiful blue colour by reflected light.

Acridine exerts a slight but distinct alkaline reaction on litmus. When inhaled, either in dust or in vapour, it causes sneezing, and, in a large quantity, coughing; the irritating action of the higher fractions of coal naphtha is probably attributable to acridine. It is exceedingly stable, not being altered by potassium hydrate, whether melted in an open vessel or heated to 280° with a small quantity of water, or by concentrated hydrochloric acid at the same temperature. It may be distilled unaltered,

\* Krant (Gmelin's *Handbook*, xvii. 177) asks, 'What becomes of the potassium acetate?'



over either ignited zinc or soda-lime. It is equally unaffected by oxidising agents; readily attacked by sodium-amalgam. Potassium dichromate and sulphuric acid convert it into a brownish-red substance, which does not yield any crystalline body. Ethyl iodide simply adds itself on to acridine, but without effecting a substitution.

The salts of acridine crystallise readily, but are not very stable, splitting up partially or wholly when boiled with water; thus the acetate is completely decomposed when its aqueous solution is evaporated, and even the sulphate and hydrochloride are partially decomposed on boiling.

Acridine does not form a carbonate, and may be precipitated in the free state from solutions of its salts by sodium carbonate. There appear to be two series of salts, all of which are yellow. The composition of some of these salts, and that of hydroacridine (*infra*) might lead to the conclusion that the true formula of acridine is  $C^{12}H^{10}N^2$ , but the vapour-density shows that it is  $C^{12}H^{11}N^2$ .

The *hydrochloride*,  $C^{12}H^{11}N^2.HCl + H^2O$ , is formed by direct combination of acridine with hydrochloric acid, the latter being in excess, and crystallises from water on cooling in brownish-yellow prismatic crystals, often several inches long. It must be washed with dilute hydrochloric acid, as it readily gives up hydrochloric acid to water. It effloresces over sulphuric acid, and at the same time its brown-yellow colour becomes pure yellow; the effloresced salt still contains two molecules of water, from which it cannot be freed without loss of hydrochloric acid. It also loses acid by long standing in the exsiccator. It is readily soluble in water, but more easily in hot than in cold; its solubility is decreased by the presence of hydrochloric acid. In alcohol it dissolves but sparingly.

The *platinochloride*,  $2(C^{12}H^{11}N^2.HCl).PtCl^4$ , is precipitated from a solution of acridine in excess of hydrochloric acid by platinic chloride, as a yellow crystalline precipitate consisting of microscopic needles. It is scarcely soluble in water, and is gradually decomposed by boiling with water. The *aurochloride*,  $C^{12}H^{11}N^2.HCl.AuCl^3$ , is prepared in a similar manner. The *mercuriochloride*,  $2(C^{12}H^{11}N^2.HCl).HgCl^2$ , is a yellow crystalline precipitate.

*Acridine periodide*,  $2(C^{12}H^{11}N^2.HI).I^2$ , is obtained as a brownish-red crystalline precipitate by adding an alcoholic solution of iodine to a solution of acridine hydriodide, and may be purified by repeated recrystallisation from hot alcohol. It forms brownish-red tables, which, by slow crystallisation, may be obtained very large, and then appear almost black. In powder it appears light brownish-red. It is easily soluble in hot alcohol, less so in cold. Water precipitates it from its alcoholic solution as a brown crystalline precipitate; the precipitate is slowly decomposed by boiling with water, iodine being liberated and acridine hydriodide passing into solution. The same decomposition is produced by treating the finely-powdered salt with a solution of sulphurous acid. A compound containing even more iodine appears to exist.

By heating acridine with *ethyl iodide*, two compounds are obtained, which, however, are difficult to purify, and have not yet been accurately examined.

The *nitrate* is readily soluble in water, and crystallises in yellow needles.

The *sulphate*,  $2C^{12}H^{11}N^2.H^2SO^4 + H^2O$ , precipitated from a boiling solution of acridine in dilute sulphuric acid on cooling (the sulphuric acid not being in great excess), forms golden-yellow needles; by slow crystallisation it is obtained in tolerably large prismatic crystals; they effloresce over sulphuric acid, but still retain one molecule of water of crystallisation, which is not given up till the temperature is raised to  $90^\circ$  or  $100^\circ$ , and then acridine sublimes. This salt is readily soluble in hot water, less so in cold, and very little soluble in alcohol. The *acid sulphate*,  $4C^{12}H^{11}N^2.3H^2SO^4$ , is precipitated by alcohol from a strong sulphuric acid solution of the base, in the form of yellow needles. It is readily soluble in water, and difficultly in alcohol; by recrystallisation from water it is converted into the neutral salt.

The *acid chromate*,  $C^{12}H^{11}N^2.H^2CrO^4$ , is the compound employed in obtaining acridine; its preparation has been already described. It is soluble in a large volume of boiling water, but nearly insoluble in cold water. By recrystallisation from water which does not contain an excess of potassium dichromate, a chromous compound is obtained. If the dry salt be heated, the base volatilises unaltered, leaving chromic oxide.

**Nitro-acridines.** Acridine warmed with nitric acid of sp. gr. about 1.45, is readily attacked, yielding, according to circumstances, mono- or di-substitution products, generally both together. These compounds are readily separated, as tetraniro-acridine does not unite with acids. On diluting with water, the dinitrated compound separates as an orange-red precipitate, while the mononitro-compounds, of which there are two, remain in solution; the last-mentioned bodies may be precipitated by ammonia, and separated by recrystallisation from alcohol.

*a-Nitroacridine*,  $C^{12}H^9(NO^2)N$ , which is the less soluble of the two, crystallises from alcohol in golden-yellow plates, resembling chloranil; it melts at  $214^\circ$  and may

be sublimed unaltered in plates. It is insoluble in water, slightly soluble in cold alcohol, rather more so in boiling alcohol, slightly in ether, and with moderate facility in chloroform. It forms salts with acids, which resemble the acridine salts, but in dilute solution they do not exhibit the beautiful blue fluorescence. The sulphate separates from a hot aqueous solution in golden-yellow crystals either acicular or prismatic; it is readily soluble in hot water, less so in cold water. The hydrochloride forms yellow prismatic crystals, easily soluble in water. The hydriodide is similar to the hydrochloride, and, like acridine hydriodide, forms a hyperiodide.

**$\beta$ -Nitroacridine** crystallises in hard plates or tables, frequently in warty masses, especially when not quite pure. In hot alcohol it is readily soluble; less so in cold alcohol, and insoluble in water. It melts at  $154^{\circ}$ . With acids it forms salts which resemble those of the preceding body.

**Dinitroacridine**,  $C^{12}H^7(NO_2)^2N$ , obtained as above described, or in greater quantity by heating acridine with a mixture of sulphuric and nitric acids for some hours in the water-bath, and is precipitated on diluting the acid liquid with water. After washing with hot water, and recrystallisation from glacial acetic acid, it is obtained in reddish-yellow tables. In alcohol, ether, and benzene, it dissolves with difficulty, more easily in boiling glacial acetic acid.

**Hydroacridine**,  $C^{12}H^{10}N^2$ , is formed by the action of sodium-amalgam on an aqueous or alcoholic solution of acridine, and may be purified from acridine by treatment with acid and solution in alcohol, the latter dissolving the hydroacridine, and leaving a white body, called 'insoluble hydroacridine.' Hydroacridine crystallises in colourless prisms, slightly soluble in cold alcohol, easily in hot alcohol and ether, but insoluble in water. It melts at  $169^{\circ}$ , and may be sublimed in prismatic crystals; when further heated it distils, but not without decomposition. It is not attacked by dilute acids, dissolves in cold concentrated sulphuric acid, and is precipitated unaltered on the addition of water. If the sulphuric acid solution be heated to  $100^{\circ}$  and then diluted, no precipitation takes place, but a yellow solution is formed, from which ammonia precipitates acridine. When it is oxidised with dilute solution of potassium dichromate and sulphuric acid, acridine chromate is precipitated, and chromium sulphate remains in solution. Sodium-amalgam converts the boiling alcoholic solution of hydroacridine for the most part into the above-mentioned insoluble hydroacridine. Hydroacridine treated with concentrated hydriodic acid yields a salt of acridine and a second base, which is either fluid or has a low melting point.

**Insoluble hydroacridine**,  $C^{12}H^{12}N^2(?)$  does not dissolve in alcohol, ether, benzene, carbon bisulphide, or chloroform; it is slowly dissolved by boiling nitrobenzene, but is, at the same time, converted into acridine. It dissolves in concentrated sulphuric acid when gently warmed, but is, at the same time, oxidised to acridine. When heated it sublimes, but the sublimate is soluble in alcohol, and consists of a mixture of acridine and hydroacridine.

**ACROLEIN**.  $C^3H^4O$ .—*Acrylic aldehyde*. According to Claus (*Deut. Chem. Ges. Ber.* iii. 401), the product obtained by the action of zinc and sulphuric acid on acrolein consists mainly of allyl alcohol,  $C^3H^5O$  (compare Linnemann, *1st Suppl.* 55). By sodium-amalgam, acrolein is almost wholly converted into the polymeric compound, hexacroleic acid,  $C^{18}H^{24}O^6$  (iii. 151).

Acrolein absorbs *cyanic acid* with avidity, and on treating the product with hydrochloric acid and leaving it to cool, the trigenic acid of the allyl series,  $C^3H^5N^3O^2$ , separates in colourless needles, which dissolve, with some difficulty, in water:

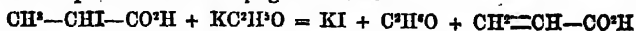


(Molms, *Zeitschr. f. Chem.* [2] vii. 27).

When *hydrogen sulphide* is passed into the acid distillate obtained by heating glycerin with potassium sulphate, a pale yellow oil separates, which congealates to a resinous mass on treatment with hydrochloric acid. It gave by analysis 40.4 p. c. carbon, 6.75 hydrogen, and 23.55 sulphur, numbers which do not lead to any simple formula (E. Mulder, *Zeitschr. f. Chem.* v. 59).

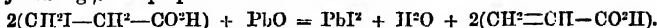
The basic product which Claus obtained by distillation of acrolein-ammonia (*1st Suppl.* 56), appears, from further investigation, to have been a mixture of picoline,  $C^8H^7N$  (obtained by Beyer, *1st Suppl.* 944), and a base, decomposed by distillation, which is either isomeric with acrolein-ammonia, or intermediate between that compound and picoline (*Ann. Ch. Pharm.* clviii. 222; *Chem. Soc. J.* [2] ix. 537).

**ACRYLIC ACID**.  $C^3H^3O^2 = CH^2=CH-CO^2H$ .—This acid is formed: 1. By heating 1 mol.  $\alpha$ -iodopropionic acid with 2 mol. potassium ethylate in a flask placed in a water-bath and provided with an upright condenser:



(von Schneider & Erlenmeyer, *Deut. Chem. Ges. Ber.* iii. 339).

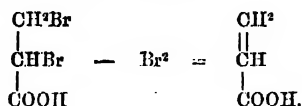
2. By heating  $\beta$ -iodopropionic acid with lead-oxide:



On the other hand, acrylic acid is completely converted into  $\beta$ -iodopropionic acid by heating it for three hours to  $100^\circ$  with concentrated hydriodic acid (Wislicenus, *Ann. Ch. Pharm.* clxvi).

3. Together with normal propyl alcohol and other products, by heating allyl alcohol with potassium hydrate (Tollens, *Zeitschr. f. Chem.* [2] vi. 457).

4. By oxidising the dibromide of allyl alcohol,  $\text{C}^3\text{H}^4\text{Br}^2\text{O}$ , with chromic or nitric acid, whereby it is converted into dibromopropionic acid,  $\text{C}^3\text{H}^4\text{Br}^2\text{O}_2$ , and debrominating this body with zinc-dust (Tollens, *ibid.* vii. 305):



Pure acrylic acid prepared from the lead-salt has a peculiar pungent odour, and boils at  $140^\circ$ – $150^\circ$ . On cooling it to  $15^\circ$ , half of the liquid solidifies to quadratic tables (Caspary a. Tollens, *Deut. Chem. Ges. Ber.* v. 560).

According to Linnemann (*Ann. Ch. Pharm.* clxii. 95), acrylic acid boils at nearly the same temperature as propionic acid, but is converted into a crystalline mass at  $+7^\circ$ , and moreover has a tendency to pass into a white amorphous mass, analogous in properties to disacryl. It combines with hydriodic, hydrobromic, and hydrochloric acids, forming substituted propionic acids. The compound with hydriodic acid is identical with the *iodopropionic acid* obtained from glycerin; that with hydrobromic acid is identical with the *isobromopropionic acid* of Richter, obtained with bromine and iodopropionic acid; but the hydrochloric acid compound melts  $20^\circ$  lower than  $\beta$ -chloropropionic acid, Wichelhaus giving the melting point of glycerin chloropropionic acid at  $65^\circ$ ; and Richter, that of the acid from iodopropionic acid and chlorine, at  $68^\circ$ ; while the acrylic acid derivative melts at  $40.5^\circ$  (corrected). The ethylic ether of this acid also boils at a higher temperature than the chloropropionic ether of Wichelhaus.

The *sodium-salt* prepared from acrylic acid, purified by fractional distillation, remains unaltered on exposure to the air. The aqueous solution of *silver acrylate* may be boiled and even evaporated to dryness at  $100^\circ$  without reduction of the silver. There are two basic acrylates of *lead*, which are soluble in water; the normal lead-salt contains water of crystallisation which is not removed by drying over sulphuric acid (Linnemann, *ibid.* 369).

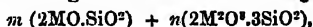
*Ethyl acrylate*,  $\text{C}^3\text{H}^5(\text{C}^2\text{H}^3)\text{O}_2$ , is easily prepared by the action of zinc and sulphuric acid on an alcoholic solution of ethylate dibromopropionate:  $\text{C}^3\text{H}^5(\text{C}^2\text{H}^3)\text{Br}^2\text{O} + \text{Zn} = \text{ZnBr}^2 + \text{C}^3\text{H}^5(\text{C}^2\text{H}^3)\text{O}_2$ . It is a colourless liquid boiling at  $100^\circ$ – $101^\circ$ , and having an extremely penetrating, but not unpleasant odour (Caspary a. Tollens).

**ADAMELLOGRANITE.** A rock belonging to the Adamello group in the Tyrol (south of the Orler). It is regarded by v. Rath as a peculiar species; but according to Baltzer (*Deut. Chem. Ges. Ber.* v. 983), it is a variety of granite.

The mica contained in it gives by analysis (after drying at  $100^\circ$ ):

SiO <sup>2</sup> .	FeO <sup>2</sup> .	Al <sup>2</sup> O <sup>3</sup> .	FeO.	MgO.	CaO.	K <sup>2</sup> O.	Na <sup>2</sup> O.
36.43	16.71	14.40	17.40	6.87	1.66	5.54	0.03 = 99.04

The oxygen ratio is  $\text{MO} : \text{M}^2\text{O}^3 : \text{SiO}^2 = 4 : 5.88 : 9.72$ , whence it may be inferred that the mica is included in the general formula of the magnesia micas—



and that it exhibits the hitherto unobserved case in which  $m = 2$ ,  $n = 1$ , so that its formula is—



It is therefore a ferrous magnesia mica, allied to Soltmann's lepidomelane (iii. 574), in which  $m = 1$ ,  $n = 1$ , and to Scheerer's magnesia mica from the zircon-syenite of Norway ( $m = 3$ ,  $n = 1$ ).

**ADAMINE.**  $4\text{ZnO.As}^2\text{O}^3 + \text{H}_2\text{O}$ .—This mineral, first obtained from Chanarcillo, in Chile, and analysed by Friedel (*1st Suppl.* 57), has also been found at Cape Garonne (Département du Var) in small crystals of the form  $\infty\text{P}$ , rarely with P, agreeing exactly in their angles with those of the Chilean mineral measured by Des Cloizeaux. The finest crystals are rose-red, others incline to green, grey, and

brown tints, and a few are white. Lenticular grains and crystalline aggregates likewise occur. One of these latter (Analysis A) agrees exactly in composition with the formula of adamine; another aggregate (B), containing a considerable quantity of copper, exhibits a transition to olivenite, with which adamine is isomorphous and with which it often occurs intergrown (Pisani, *Compt. rend.* lxx. 1001). Analysis C is by Damour (*ibid.* lxxvii. 1124):

	As <sup>2</sup> O <sup>3</sup>	ZnO	CuO	CoO	CaO	H <sup>2</sup> O
A. 38.50	52.50	—	3.92	—	3.57	= 98.49
B. 39.85	31.85	23.45	0.52	0.87	3.68	= 100.22
C. 39.24	49.11	1.75	5.16	—	4.25	= 99.51

The specimen C also contains traces of ferric oxide.

**ADIPIC ACID.**  $C^6H^{10}O^4$ .—The ordinary or a modification of this acid,  $(C_6H_7O_2)_2$ , which Wislicenus obtained in small quantity by the action of finely divided silver or copper on  $\beta$ -iodopropionic acid (*1st Suppl.* 58), is produced much more abundantly by similar treatment of  $\alpha$ -bromopropionic acid. With silver the action takes place at ordinary temperatures, and is attended with considerable evolution of heat; with copper application of heat is necessary. The reaction in either case having been completed at  $150^\circ$ – $160^\circ$ , the adipic acid may be extracted from the product by water, and purified by neutralising with ammonia, precipitating with basic lead acetate, and decomposing the lead salt with hydrogen sulphide. The filtrate evaporated over the water-bath leaves a strongly acid syrup, which exhibits signs of incipient crystallisation only after standing for some months over oil of vitriol. The solution of the neutral ammonium salt gives off on evaporation a large quantity of ammonia, and is converted into the extremely soluble acid salt; when recently prepared, this solution gives a gummy precipitate with ferric salts, and a flocculent precipitate with lead salts. The lead salt, which soon becomes denser, has the composition  $C^6H^4PbO^4$  (Wislicenus, *Deut. Chem. Ges. Ber.* ii. 720).

The same acid is readily formed by treating hydromuconic acid,  $C^6H^8O^4$ , with water and a large quantity of sodium-amalgam (Lamprecht, *Ann. Ch. Pharm.* clxv. 253).

Adipic acid is also produced, together with acetic and carbonic acids, by oxidation of phorono with chromic acid (Kachler, *ibid.* clxiv. 75):



**Bromadipic acids.**—*Monobromadipic acid*,  $C^6H^9BrO^4$ , is obtained by heating 1 mol. adipic acid with 2 atoms bromine to  $160^\circ$  in sealed tubes. It is a solid, dark-coloured body, having an odour of camphor, very soluble in ether, and partially decomposed by water. By boiling with potash it is converted into a dipomallic acid,  $C^6H^{10}O^3$ .

*Dibromadipic acid*,  $C^6H^7Br_2O^4$ , is produced by heating 1 mol. adipic acid with 4 at. bromine, in sealed tubes, to  $170^\circ$ ; if this temperature is exceeded the mass becomes carbonised. It is a yellowish, pulverulent, unstable substance smelling like camphor; dissolves easily, but with decomposition, in water, and after two crystallisations retains only 9.3 (instead of 52.6) pure bromine. When heated with water to  $160^\circ$  for some hours, it is converted into adipotartaric acid,  $C^6H^{10}O^6$  (H. Gal and J. Gay-Lussac, *Compt. rend.* lxx. 1175).

The same, or an isomeric acid, is contained in the mother-liquors of bromhydromuconic acid (produced by adding bromine to a hot aqueous solution of hydromuconic acid), and is obtained in larger quantity by adding bromine to a hot saturated solution of bromhydromuconic acid. It has not been isolated from these liquors, but its existence was proved by the action of silver oxide on its aqueous solution whereby it is converted into dioxyadipic acid,  $C^6H^{10}O^6$  (Limpricht).

*Isodibromadipic acid* is formed by adding bromine to a warm solution of hydromuconic acid in glacial acetic acid. It is readily soluble in alcohol, ether, and hot water, sparingly in cold water, and crystallises in nodular groups of white needles. Between  $175^\circ$  and  $190^\circ$ , it melts and decomposes with ebullition. The *barium salt*,  $C^6H^7Br_2BaO^4 + H^2O$ , is an indistinct crystalline mass. The acid heated with water and sodium-amalgam is reconverted into hydromuconic acid (Limpricht).

*Tribromadipic acid*,  $C^6H^5Br_3O^4$ , is formed by adding bromine to a solution of hydromuconic acid heated on a water-bath. A colourless oil, smelling like pepper, then separates out, and the watery liquid on standing deposits tribromadipic acid in small white needles, melting at  $177^\circ$ – $180^\circ$ . Its solution boiled with baryta-water yields the barium salt of trioxadipic acid,  $C^6H^4O^7$  (Limpricht).

*Tetrabromadipic acid*,  $C^6H^3Br_4O^4$ , is formed in small quantity when 1 mol. of hydromuconic acid is heated with 3 mols. bromine and some water to  $100^\circ$  for seven hours;

a large quantity of carbon dioxide and the pungent oil above mentioned are formed at the same time. The acid dissolves sparingly in water, easily in alcohol and ether, and is decomposed when its alcoholic solution is boiled, yielding a volatile compound which has an ethereal odour. When heated to  $200^{\circ}$ – $211^{\circ}$ , it melts and blackens (Limpricht).

**Oxyadipic acids.**—*Monooxyadipic*, or *Adipomalic acid*,  $C^{11}H^{10}O^3 = C^{11}H^9(HO)O^3$ , is prepared by treating monobromadipic acid with potash, decomposing the resulting potassium-salt with hydrochloric acid, and extracting with alcohol, and remains, on evaporating the alcoholic solution, as a light yellow acid liquid, which, after some time, is partly converted into an indistinctly crystalline mass. The aqueous solution gives with lead acetate a white precipitate, which melts when the liquid is heated, and solidifies on cooling to a somewhat hard brownish mass. This lead salt dissolves in a small quantity of a hot solution of lead acetate, and separates therefrom in nacreous scales having the composition  $C^8H^7PbO^3 + 5H^2O$ . When decomposed with hydrogen sulphide, it yields a viscid mass exactly like the original acid. The ammonium salt crystallises imperfectly; the potassium salt not at all (Gal a. Gay-Lussac, *loc. cit.*).

*Dioxyadipic acid*,  $C^{11}H^8O^4$ , is produced, as above stated, by the action of silver oxide on the aqueous solution of dibromadipic acid, and remains on evaporation as an uncrystallisable syrup soluble in alcohol and ether. The barium salt is formed by boiling a solution of dibromadipic acid with baryta-water. It is very soluble in water, and is precipitated by alcohol as a hygroscopic crystalline powder,  $C^{11}H^6BaO^4 + 4H^2O$ , which loses half its water at  $150^{\circ}$ , and begins to decompose at  $160^{\circ}$ . Its solution is precipitated by lead and silver salts (Limpricht).

An acid isomeric with this, and called adipotartaric acid, is produced by heating pulverulent dibromadipic acid with water to  $150^{\circ}$  for several hours, and evaporating. It tastes like the fruit-acids, is moderately soluble in alcohol and ether, much more soluble in boiling than in cold water, and always separates from solution in well-defined monoclinic laminae. It has no action on polarised light. Its solution, agitated with potash-ley, yields a crystalline precipitate resembling cream of tartar. With ammonia it forms salts which crystallise with facility (Gal a. Gay-Lussac).

*Trioxadipic acid*,  $C^{11}H^6O^5$ .—The barium salt of this acid is formed by boiling tribromadipic acid with baryta-water. It is very soluble in water, and remains on evaporation as an amorphous transparent mass, and is precipitated by alcohol as a light white powder,  $4C^{11}H^4BaO^5 + 3H^2O$ , which loses one-third of its water at  $85^{\circ}$ , being reduced to  $2C^{11}H^4BaO^5 + H^2O$ . Its aqueous solution gives white precipitates with lead and silver salts, reddish-yellow with ferric salts.

The *free acid*, separated from the barium salt by sulphuric acid, is readily soluble in water and in alcohol. By adding alcohol and benzene to its concentrated aqueous solution, and leaving it to evaporate slowly, it is obtained in prisms. Its alcoholic solution turns red on evaporation, without yielding crystals, and the aqueous solution becomes yellowish-brown and colours the skin intensely yellow (Limpricht).

**ÆSCULIN**,  $C^{11}H^{10}O^3$ , and **ÆSCULETIN**,  $C^{11}H^8O^4$  (Schiff, *Deut. Chem. Ges. Ber.* iii. 366; iv. 472).—Æsculin is converted by acetic anhydride into hexacetylæsculin,  $C^{18}H^{16}(C^2H^3O)^6O^3$ , and by aniline into trianilæsculin,  $C^{18}H^{10}O^4(C^6H^5.N)^3$ .—Æsculetin, treated with acetic anhydride, yields well-crystallised triacetylæsculetin,  $C^{11}H^6(C^2H^3O)^3O^4$ , a compound previously obtained by Nachbaur (*Ann. Ch. Pharm.* cvii. 248). Aniline acts readily on æsculetin, and by heating the two bodies together to  $200^{\circ}$  trianilæsculetin,  $C^{11}H^8O(C^6H^5.N)^3$ , is ultimately obtained in the form of a brown amorphous powder soluble with red colour in alcohol.

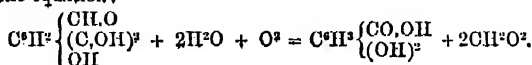
Paræsculetin (1st *Suppl.* 59) has the properties of an aldehyde, and acts as a powerful deoxidising agent, reducing alkaline cupric tartrate, indigo, silver-salts, &c., in the cold. It is acted upon by aniline more easily than æsculetin, likewise yielding trianilæsculetin as ultimate product. It is not acted upon by acetic anhydride.

The above reactions may be explained by the following constitutional formulæ:—

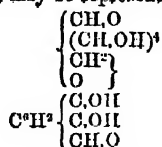


In the conversion of paræsculetin into trianilæsculetin, the 3 atoms of aldehydic oxygen are directly replaced by the bivalent imidogen group  $NC^6H^5$ , whereas in the case of æsculetin, the alcoholic groups  $C.OH$  must first be converted, under the influence of the high temperature, into the aldehydic groups  $CH.O$ ; hence the greater facility of the transformation in the former case.

By fusion with potash, æsculetin is converted into formic and protocatechuic acids, according to the equation:



The constitution of æsculin may be represented by the formula:



**AGARIC.** Some agarics contain mannite; others mycose or trehalose (iii. 1068); others again contain both these sugars in very variable proportions; and some contain mannite, trehalose, and another sugar, the nature of which has not yet been fully determined. Botanical analogy affords no guide to the kind of sugar present, for in species closely allied, growing in the same soil and under the same conditions, some contain mannite only and others trehalose only (A. Muntz, *Compt. rend.* lxxvi. 649).

*Agaricus fatus* contains, according to Taci (*ibid.* 505), 67·20 p. c. water, 0·60 mannite, 0·09 pectic acid, 4·65 fibrin, 1·55 bassorin, 20·09 ligucous matter, 0·68 fat, acids, colouring and odorous matter, and 5·13 ash.

The larch-agaric (*Boletus Laricis*) pulverised, dried, and treated with pure anhydrous ether, yields two substances, viz.: 1. A red-brown amorphous substance, called agaric resin, soluble in alcohol, wood-spirit, chloroform, and acetic acid, insoluble in benzene and carbon bisulphide, and said to have the composition  $C^{51}H^{92}O^{10}$ .—2. Agaricic acid, which crystallises in tufts of needles, melts at  $145^{\circ}$ , gives off water and turns brown at a somewhat higher temperature. It dissolves very easily in alcohol, less easily in chloroform, very sparingly in ether and acetic acid, still less in carbon bisulphide and benzene. When the alcoholic solution is distilled, the acid volatilises with the alcohol vapour. Its sodium-salt is precipitated by alcohol in amorphous flocks which, in the course of 24 hours, change to long needles, often united in concentric groups. Metallic salts give, with the dilute solutions, mostly crystalline precipitates (Fleury, *J. Pharm.* [4] x. 202).

**AGONIADIN.** A non-azotised, crystalline bitter substance, extracted, together with tannic acids, resins, &c., from Agoniada bark (the bark of *Plumeria lanceifolia*), which is used in Brazil as a remedy for intermittent fever. It separates from dilute solutions in stellate groups of needles having a silky lustre; from concentrated solutions in warty groups of crystals. It melts when heated, but does not sublime. It is inodorous, very bitter, nearly insoluble in ether, easily in ether-alcohol, carbon bisulphide, and hot alcohol. Cold water dissolves only traces of it; boiling water dissolves it immediately, and deposits it in white flocks on cooling. It dissolves easily in potash and ammonia. Strong sulphuric acid dissolves it with gold-yellow colour, which after a while passes into greenish. On addition of fuming nitric acid, this solution passes into dark yellow, and deposits yellow crystalline flocks. Dilute sulphuric acid dissolves agoniadin only when warmed; the solution becomes coloured on boiling, and then exhibits the reactions of sugar. Agoniadin is allied in composition to arbutin, but not identical with it. From an analysis by Geuther, it appears to have the composition  $C^{10}H^{14}O^4$  (Peckolt, *Arch. Pharm.* [2] cxlii. 34).

**ALANINE, or AMIDOLACTIC ACID,**  $C^3H^7NO^2$ , is produced, together with lactic acid, by boiling  $\alpha$ -chloropropionic acid with aqueous ammonia. See LACTIC ACID.

**ALBITE.** See FELSPAR.

**ALBUMIN.** See PROTEÏDS.

**ALCOHOLS.** 1. *Simultaneous distillation of Water and certain Alcohols insoluble in Water.*—When a mixture of amylic alcohol and water is submitted to distillation, ebullition begins at  $96^{\circ}$ , and remains remarkably constant at this point; so long as these temperatures remain constant, the volumes of water and of amylic alcohol condensed during any given time are invariably in a constant ratio, viz. 2 to 3, and the temperature does not begin to rise until either the water or the alcohol has wholly distilled over, leaving a surplus of alcohol or of water (as the case may be) in the retort; if the water was originally more than two-thirds of the volume of the alcohol, the temperature rises to  $100^{\circ}$  as soon as the whole of the alcohol has distilled over; but if less than the two-thirds of water was originally present, the boiling

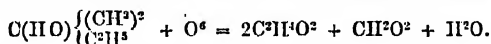
point rises to  $130^{\circ}$  as soon as the whole of the water has distilled over, amylie alcohol only being then left.

Butylic alcohol gives precisely analogous results, the volumetric ratio in this case being 1 of water to 5 of alcohol; the boiling point of the mixture is perfectly constant at  $90.5^{\circ}$ , i.e.  $9.5^{\circ}$  below the boiling point of water, and  $17.5^{\circ}$  below that of butylic alcohol; fourteen experiments gave absolutely the same numbers in each instance.

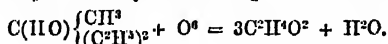
When a mixture of water, butylic, and amylie alcohols is used, the temperature of ebullition is not constant, but regularly rises; the temperature, however, always lies between  $90.5^{\circ}$  and  $96^{\circ}$ , being higher the larger the proportion of amylie alcohol present; the relative volume of water that distils over also continually increases, being, however, always greater than  $\frac{1}{2}$ th of the total volume that passes over, and less than  $\frac{2}{3}$ ths—i.e. lying between the relative numbers found with butylic alcohol and water, and with amylie alcohol and water (Pierre a. Puchot, *Compt. rend.* lxxiii. 599).

2. *Oxidation of Tertiary Alcohols.*—In the oxidation of these alcohols, as in that of the ketones, the simplest, or one of the simplest of the three alcohol-radicles present remains united to the carbon-atom which binds together the whole group, forming an acid  $C^3H^3O^2$ , while each of the other two alcohol-radicles is separately oxidised, yielding (if it is a primary radicle) an acid containing the same number of carbon-atoms as itself; formic acid, however, in this, as in similar cases, is not actually eliminated, but is further oxidised to carbonic acid.

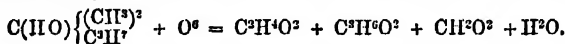
*Dimethyl-ethyl carbinol* yields in this manner, acetic acid and carbon dioxide:



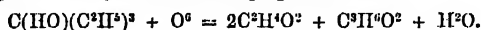
*Methyl-diethyl carbinol* yields nothing but acetic acid:



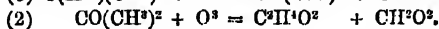
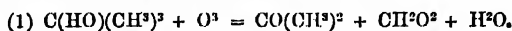
*Dimethyl-propyl carbinol* gives acetic and propionic acids, together with formic or carbonic acid:



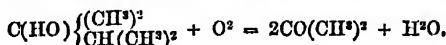
*Triethyl carbinol* gives acetic and propionic acids:



Exceptions to this law of oxidation appear to be furnished by *trimethyl carbinol* and *dimethyl-isopropyl carbinol*, the former of which yields acetone, acetic acid, and, according to former experiments, propionic acid (*1st Suppl.* 66), while the latter yields nothing but acetone. The formation of acetone from trimethyl carbinol may be regarded as an intermediate stage in the oxidation, thus:



In the case of dimethyl-isopropyl carbinol, the oxidation of the simpler alcohol-radicle appears to stop at the first stage—that is to say, at the formation of acetone and the more complex radicle; the isopropyl, being a secondary radicle, is likewise oxidised, not to an acid, but to acetone; hence acetone is the only product:



The formation of propionic acid from trimethyl carbinol, which would be completely at variance with the law above stated, was inferred in the earlier experiments from the composition of a silver salt; but subsequent examination has shown that the supposed propionate of silver was really a mixture of acetate and isobutyrate. The formation of isobutyric acid is not at variance with the above law; it is formed by a molecular change corresponding to that by which Linnemann has found that derivatives of trimethyl carbinol are obtained from isobutyl alcohol (Butlerow, *Zeitschr. f. Chem.* [2] vii. 484).

3. *Formation of Monatomic and Hexatomic Alcohols from Glucose and Milk-sugar.*—When glucose is treated with sodium-amalgam containing 3 p. c. sodium, and the alkaline liquid is neutralised with sulphuric acid, then distilled and treated with potassium carbonate, an oily layer is obtained, consisting of ethylic, isopropylic and hexylic alcohols. The liquid remaining in the retort contains a large quantity of mannite.

Milk-sugar, similarly treated, yields ethylic, isopropylic and hexylic alcohols, the residuo containing dulcitol. Inverted milk-sugar yields the same products, together with mannite (G. Bouchardat, *Compt. rend.* lxxiii. 108).

4. On the formation of Alcohols from the corresponding Fatty Acids, see BUTYL, ETHYL, and PROPYL Alcohols.

5. On a class of bodies intermediate between Alcohols and Aldehydes, see ALDEHYDE-ALCOHOLS.

6. On the Thermal Effects of the combination of Alcohols with Bases, see HEAT.

**ALDANE.** A term proposed by Riban (*Compt. rend.* lxxv. 98) to designate products formed by the union of two or more molecules of an aldehyde, with elimination of water—e.g. crotonic aldehyde,  $C^6H^{10}O^2 = 3$  mol. acetic aldehyde, minus 1 mol. water. The prefixes *di*, *tri*, &c., may be used to denote the number of aldehyde molecules thus condensed—e.g. *diacetalthane*, *triacetalthane*, *divineralthane*, &c.

**ALDEHYDE**,  $CH^3.CHO$ , is formed:  $\alpha$ . By oxidation of ethylene with aqueous chromic acid at  $120^\circ$ ; at ordinary temperatures no action takes place (Berthelot, *Compt. rend.* lxxviii. 334).

$\beta$ . By inverse substitution from chloral,  $CCl^3.CHO$ , when clippings of zinc are introduced into a solution of that substance slightly acidulated with sulphuric or hydrochloric acid. Considerable quantities of the polymerides of aldehyde, especially paraldehyde, are formed at the same time (Personne, *Compt. rend.* lxxi. 227).

$\gamma$ . In the electrolysis of sugar-solutions acidulated with sulphuric acid (H. T. Brown, *Chem. Soc. J.* [2] x. 578).

$\delta$ . In vinous fermentation. See FERMENTATION.

Aldehyde occurs, together with metalddehyde and paraldehyde, in the 'first runnings' obtained in the manufacture of alcohol from sugar-beet and from potatoes (Krämer a. Pinner, *Deut. Chem. Ges. Ber.* ii. 403; Kekulé, *ibid.* iv. 718). Krämer and Pinner also find acetal and crotonic aldehyde in these runnings (*ibid.* iii. 75). They attribute the formation of the aldehyde to oxidation of the alcohol on the carbon filters. Kekulé, on the other hand, attributes it—at least in the case of alcohol from sugar-beet—to the oxidising action of nitrates which are present in considerable quantity in the liquors. To this Krämer and Pinner reply (*ibid.* iv. 787) that the oxidation of the alcohol to aldehyde cannot be due in all cases to the action of nitrates, since the quantity of those salts in some cases, as in the first runnings from potato-spirit, is too small to account for the quantity of aldehyde produced. Moreover, considerable heating of the carbon-cylinders is observed on passing the spirit through them (compare 1st *Suppl.* p. 213).

Aldehyde, mixed with *pyrogallie acid* and hydrochloric acid and gently warmed, produces a red coloration, becoming violet on addition of an alkali. A mixture of aldehyde and *phenol* also gives a red colour when warmed with sulphuric acid (A. Bayer, *Deut. Chem. Ges. Ber.* v. 25).

Aldehyde, heated with *acetamide* in sealed tubes, yields the compound  $CH^3CH(NH.C^2H^3O)$ , which crystallises in large prisms, melts at  $169^\circ$ , distils with partial decomposition, and gives up the aldehyde when treated with acids (Tawildarow, *Deut. Chem. Ges. Ber.* v. 477).

On the action of *bromine* on aldehyde, see page 36; on the action of *chlorine*, see CROTONIC CHLORAL.

#### *Polymeric modifications of Aldehyde.*

Five of these modifications have been described by different chemists, viz.:—1. A liquid modification boiling at  $94^\circ$ , accidentally obtained by Liebig.—2. A modification called *olaldehyde*, melting at  $+2^\circ$  and boiling at  $94^\circ$ , which Fehling accidentally obtained by exposing aldehyde to a winter temperature.—3. A liquid modification boiling at  $125^\circ$ , which Weidenbusch obtained by the action of very dilute sulphuric acid or nitric acid on aldehyde, and for which Gerhardt suggested the name *paraldehyde*.—4. Infusible but sublimable *metalddehyde*, discovered by Liebig, and further examined by Fehling and Weidenbusch.—5. *Acetaldehyde*, produced by the action of zinc chloride on glycol or aldehyde, first obtained by Wurtz, further examined by Bauer (i. 109; iv. 349; 1st *Suppl.* 76).

Recent investigations have, however, considerably reduced the number of these modifications. The liquid called *acetaldehyde* has been shown by Kekulé to be resolvable by heat into water and crotonic aldehyde; and Wurtz has recently shown that it is not a true polymeride of aldehyde, but a compound intermediate in properties and constitution between aldehyde and alcohol; it will be described in a separate article under the name of *aldol*. The modifications described by Fehling and by Weidenbusch have been shown by Gauthier a. Cartmel (*Ann. Ch. Pharm.* cxii. 16),



and by Lieben (*ibid. Suppl. i. 14*) to be identical with each other and with the modification (paraldehyde) melting at  $10-12^{\circ}$  and boiling at  $124^{\circ}$ , which the former chemists obtained by the action of sulphurous acid, the latter by that of ethyl iodide upon aldehyde; and, finally, it has been shown by Kekulé & Zincke (*Ann. Chem. Pharm.* clxii. 141; *Deut. Chem. Ges. Ber.* iii. 468), that, besides ordinary aldehyde, there are but two distinct modifications, viz.—1. Paraldehyde, fusible and distillable;—2. Metaldehyde, infusible, but sublimable. These chemists find, in accordance with the observations of Gauthier & Cartmell, that carefully purified aldehyde suffers no change either by long keeping or by continued heating or cooling, polymerisation being due in all cases to the presence of some foreign substances which appear to exert a kind of fermentative action. In most cases both modifications are formed together, metaldehyde chiefly in the cold, paraldehyde at ordinary or at higher temperatures.

**Paraldehyde.** In presence of a very small quantity of hydrochloric acid, chlorocarbonic oxide, or sulphurous anhydride, aldehyde gradually becomes hot, the temperature frequently rising to  $38^{\circ}$  or  $40^{\circ}$ . Both zinc chloride and sulphuric acid act in the same way, the addition of a drop of the concentrated acid causing explosive ebullition of the aldehyde; the action of the dilute acid is less energetic. In all these reactions an almost complete transformation into paraldehyde occurs, as is indicated by the change in specific gravity ( $0.986$  at  $15^{\circ}$ ), but the pure substance cannot be directly separated from the product by rectification, as much aldehyde is then regenerated. The best method of separation is to cool the liquid to  $0^{\circ}$ , when the paraldehyde crystallises out, and may be collected and purified by distillation.

Paraldehyde is a colourless liquid of peculiar odour, resembling that of acetal. It boils at  $124^{\circ}$ , and crystallises when cooled below  $10^{\circ}$ , forming large transparent prisms, which melt at  $10.5^{\circ}$ . Its specific gravity at  $15^{\circ}$  is  $0.998$ , and its vapour-density three times that of ordinary aldehyde. It is less soluble in hot than in cold water; 100 parts of the latter dissolving 12 parts at  $13^{\circ}$ . Distillation with sulphuric acid, hydrochloric acid, zinc chloride, or chlorocarbonic oxide, reconverts it into aldehyde. When subjected to the action of phosphorus pentachloride, it yields ethylidene chloride, as observed by Gauthier (*Zeitschr. f. Chem.* 1865, 32), and with hydrochloric acid it gives the same ethylidene oxychloride that Lieben obtained from ordinary aldehyde (*Ann. Chem. Pharm.* cvi. 336).

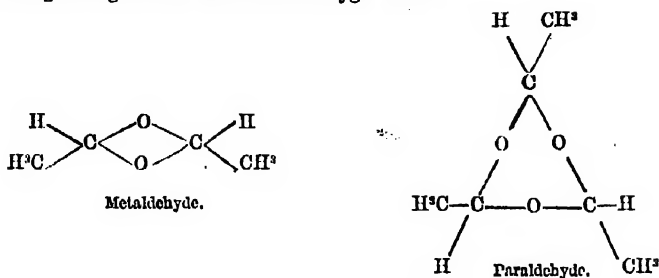
The so-called chloracetone, isomeric with vinyl chloride,  $C^2H^3Cl$ , which Haritzky obtained some years ago (*Ann. Chem. Pharm.* cxi. 192), by the action of phosgene on aldehyde, appears, from the experiments of Kekulé & Zincke, to be nothing but a mixture of aldehyde and paraldehyde with a small quantity of phosgene, and is completely converted into aldehyde by passing its vapour over heated quicklime.

**Metaldehyde.** This modification, hitherto obtained only accidentally, has been shown by Kekulé & Zincke to be formed from aldehyde at a low temperature by the same reagents that cause the formation of paraldehyde at a comparatively high temperature. To prepare it in quantity, a few bubbles of hydrochloric acid or sulphurous acid are passed into aldehyde cooled in a freezing mixture, the metaldehyde which crystallises out on standing is removed, and the mother-liquors are submitted to distillation, the distillate being collected in a well cooled receiver; more metaldehyde is then deposited, which is again removed, and the distillation, &c., repeated as above. Calcium chloride effects the same transformation at the ordinary temperature. Metaldehyde crystallises in fine white needles, and that produced by calcium chloride in short, thick transparent prisms belonging to the quadrate system. It is insoluble in water, and but slightly soluble in alcohol, ether, chloroform, or benzene. When heated it sublimates, but ordinary aldehyde is always formed at the same time. Heated to  $112^{\circ}$  to  $115^{\circ}$  in a closed tube, it is completely converted into aldehyde, and the same change is produced by distillation with dilute sulphuric acid. With phosphorus pentachloride it forms ethylidene chloride.

As the vapour-density of metaldehyde cannot be determined, on account of its partial conversion by heat into ordinary aldehyde, and as none of its known reactions give any information as to its molecular weight, it is impossible at present to form any definite idea of its constitution. But the formation of ethylidene chloride and the ready conversion into aldehyde render it probable that this modification consists of several (perhaps two) aldehyde molecules united into one by their oxygen-atoms.

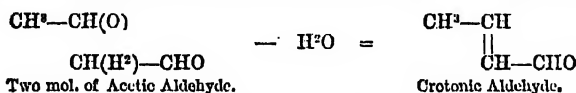
As paraldehyde has three times the vapour-density of aldehyde, its molecular formula is  $C^3H^4O^3$ , and its reaction with phosphorus pentachloride, with hydrochloric acid, sulphuric acid, and generally with all ferment-like bodies, which easily convert it

into aldehyde, suggest that the three aldehyde molecules contained in it are united into a ring through the medium of their oxygen-atoms.



### Condensation-products of Aldehyde.

**I. Condensation with Separation of Water.** (Kekulé, *Ann. Chem. Pharm.* clxii. 92-124.) — The formation of crotonic aldehyde by heating acetic aldehyde with zinc chloride, is mentioned in the First Supplement (p. 513), where crotonic aldehyde is represented by the formula  $\text{CH}^2=\text{CH}-\text{CH}^2-\text{CHO}$ . Kekulé, however, now takes a somewhat different view of the mode of transformation, leading to the representation of crotonic aldehyde by the formula  $\text{CH}^2=\text{CH}-\text{CH}=\text{CHO}$ , as shown by the following equation, in which the eliminated atoms are enclosed in brackets:—



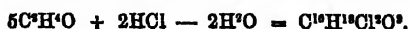
The same transformation is effected by the action of hydrochloric acid, other products being however formed at the same time, viz., chlorobutyric aldehyde  $\text{C}^4\text{H}^7\text{ClO}$ , resulting from the combination of part of the crotonic aldehyde with hydrochloric acid—the same compound being in fact producible by saturating crotonic aldehyde with hydrochloric acid gas; and a chlorinated compound  $\text{C}^{10}\text{H}^{16}\text{Cl}^2\text{O}^2$ , besides higher condensation-products. The manner in which these several compounds are obtained is as follows:—

When aldehyde is saturated in a cooled vessel with hydrochloric acid, and then left to itself for about two days, two layers of liquid form, the lower of which consists of aqueous hydrochloric acid. On removing the upper layer and distilling immediately, torrents of hydrochloric acid gas escape, and a pungent oil heavier than water passes over, whilst a large portion remains behind as a non-volatile viscid mass. If the upper layer be washed with water previous to distillation, the general course of the action is the same, but the quantity of viscid residuo is less. Still better results are obtained by distilling the washed oil in a stream of hydrogen, and adding marble to neutralise the free acid.

Crotonic aldehyde is easily obtained from all the distillates by rectification; its quantity is, however, relatively small, and smaller as the aldehyde saturated with hydrochloric acid has been left to stand for a longer time. If the crude oils have been washed with water, considerable quantities of tolerably pure crotonic aldehyde may be obtained from this water by distillation.

If the distillation of the oil, after washing with water or with alkali, be performed by means of steam, the viscid residuo deposits needle-shaped crystals of chlorobutyric aldehyde  $\text{C}^4\text{H}^7\text{ClO}$ ; the quantity of which increases on adding alcohol, and leaving the liquid to itself for some days.

If the receivers be occasionally changed during the distillation with steam, the earlier distillates contain chiefly crotonic aldehyde, the latter ones an oil which sinks in water. The oil of the last distillates, deposits, sometimes immediately, sometimes after a few days, laminar crystals of the chlorinated compound  $\text{C}^{10}\text{H}^{16}\text{Cl}^2\text{O}^2$ ; the empirical relation of which to aldehyde may be represented by the equation:



This compound forms broad nacreous rhombic plates or tables, sometimes larger well-developed crystals. It melts at  $98^\circ$ , and volatilises easily with vapour of water.

It is insoluble in water, but slightly soluble in cold alcohol, easily soluble in hot alcohol and in ether.

*Higher Condensation-products.*—Both the liquid of higher boiling-point which remained after distilling off the crotonic aldehyde as above described, and a product obtained by heating crotonic aldehyde with twice its weight of aldehyde and some zinc chloride to  $100^{\circ}$  for 96 hours, yielded, by distillation with steam and subsequent rectification, an oily product, boiling at about  $172^{\circ}$ , and having nearly the composition  $C^8H^{10}O$ . On exposing small quantities of this oil to the air, crystalline needles were formed, and on boiling it with water and silver oxide, a crystalline, difficultly soluble silver salt was produced, containing an amount of silver closely corresponding with the formula  $C^8H^7AgO_2$ . This oil was probably the triple condensation-product of aldehyde:  $3C^2H^3O - 2H^2O = C^8H^{10}O$ . On rectification of the products of still higher boiling-point, an oil was separated, having nearly the composition  $C^{12}H^{16}O = 4C^2H^3O - 3H^2O$ .

The mode of action of zinc chloride, and of the numerous other salts which exert the above described condensing action on aldehyde, may be explained on the otherwise probable assumption that, in an aqueous solution of zinc chloride, there are present besides the hydrated molecules, a certain number of anhydrous molecules, these latter being always in motion, and constantly changing their condition, the hydrated molecules becoming anhydrous, the anhydrous molecules becoming hydrated, in such a way, however, that a mean condition of equilibrium is always preserved. If then bodies are present from which the elements of water can be withdrawn, a certain, although probably small, proportion of those molecules which are in the act of taking up water, cause the separation of water from these substances, and combine with the water thus separated, so that in course of time a very small quantity of such an agent is capable of performing a large amount of work. It is evident that heat is not absolutely necessary for the production of such reactions, although an increase of temperature has an accelerating influence. In fact, aldehyde mixed with zinc chloride undergoes the same change in a few weeks at summer temperature, and in some months at autumn and winter temperatures, as when heated for several hours to  $100^{\circ}$ . The action of zinc chloride and similar salts might also be referred to the presence of hydrochloric acid: for an aqueous solution of the former may be supposed to contain free hydrochloric acid and free zinc oxide.

Similar considerations apply to the decomposition of complex compounds with assumption of the elements of water. Thus, that of the glucosides in presence of traces of sulphuric acid may probably be referred to an action of the same nature.

According to Paternò a. Amato, aldehyde is converted into crotonic aldehyde by heating with *ethylidene chloride* (I. Suppl. 513). According to Kekulé, however, (*Deut. Chem. Ges. Ber.* iii. 135), this is the case only when the ethyldiene chloride contains free hydrochloric acid. Pure ethyldiene chloride has no action whatever on aldehyde, but a mere trace of hydrochloric acid is sufficient to produce the condensation. This conclusion is confirmed by the experiments of Krämer a. Pinner (*ibid.* 76 and 390), who find that ethyldiene chloride heated with aldehyde does not undergo the slightest alteration.

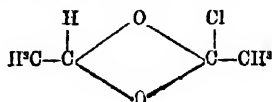
*Chlorinated Condensation-products.*—Krämer a. Pinner (*Ann. Chem. Pharm.* clviii. 37), by passing chlorine into aldehyde, at first cooled by a freezing mixture, but heated to  $100^{\circ}$  at the close of the reaction, obtained in about 24 hours a semi-solid brown mass, which, when distilled, yielded between  $160^{\circ}$  and  $180^{\circ}$ , a liquid from which, by subsequent fractional distillation, trichlorocrotonic aldehyde or crotonic chloral  $C^4H^3Cl_3O$  was obtained, boiling at  $163^{\circ}$  to  $165^{\circ}$ . The chlorine first takes hydrogen from a portion of the aldehyde, forming hydrochloric acid; this acts on the rest of the aldehyde in the manner above described, forming crotonic aldehyde; and the latter is converted by the excess of chlorine into trichlorocrotonic aldehyde (I. Suppl. p. 513). By adding fragments of marble so as to remove the hydrochloric acid as fast as it is formed, a distillate is obtained exhibiting the properties of ordinary chloral (Pinner, *Deut. Chem. Ges. Ber.* iv. 256).

Wurtz (*Ann. Chem. Phys.* [3] xlix. 58), by passing chlorine into aldehyde obtained acetyl chloride and a body  $C^4H^3ClO_2$  containing the elements of acetyl chloride and aldehyde, and producible by their direct combination. Krämer a. Pinner were not able to obtain these substances, but Wurtz (*Compt. rend.*, lxxiii. 528) has recently made further experiments which corroborate his former results.

By passing chlorine through an ice-cold mixture of carbon perchloride and one-tenth of its weight of aldehyde, in sunshine, till the liquid becomes strongly yellow, he obtains a product which, on agitation with mercury and distillation, gives off hydrochloric acid, and yields, after fractionating several times, a liquid boiling below  $70^{\circ}$ , and another boiling at about  $120^{\circ}$ . The first is a mixture of acetyl chloride and

carbon perchloride; the second contains the compound  $C^4H^2ClO^2$ , which, treated with water, yields acetic and hydrochloric acid, and apparently also aldehyde, whence it appears to contain the elements of aldehyde and acetyl chloride condensed: probably thus

either as



**II. Condensation with Addition of Hydrogen.** (Kokulé, *Ann. Chem. Pharm.* cxlii, 305-320).—When an acidulated dilute aqueous solution of aldehyde is treated with sodium amalgam, butylene-glycol  $C^4H^{10}O^2$  is formed in small quantity, according to the equation  $2C^2H^4O + H^2 = C^4H^{10}O^2$ ; the reaction being analogous to that by which benzoic aldehyde  $C^7H^6O$  is converted into hydrobenzoin,  $C^{10}H^{14}O^2$ .

The butylene-glycol thus obtained is different from ordinary butylene-glycol; it boils at  $203.5^\circ-204^\circ$ , and yields by oxidation with nitric and crotonic aldehyde, acetic acid and oxalic acid, whence it is inferred to have the constitution represented by the formula  $CH^2(OH)-CH^2-CH(OH)CH^2$ . (See BUTYLENE-COMPOUNDS.)

#### *Substitution-products of Aldehyde.*

**Dibromaldehyde**,  $C^2H^2Br^2O$ , is produced by the regulated action of bromine on aldehyde. It crystallises in long needles, soluble in water, alcohol, and ether, has a pungent, tear-exciting odour, and reduces silver nitrate. The action of bromine on aldehyde under slightly different circumstances, gives rise to dibromacetic acid (Haarmann, *Deut. Chem. Ges. Ber.* iii, 758).

**Monochloraldehyde**,  $C^2H^2ClO$  (Glinsky, *Zeitschr. f. Chem.* vi, 647).—This compound is produced by the action of hypochlorous acid on vinyl chloride  $C^2H^3Cl$  (*I. Suppl.* 76). When this gas is passed into a cooled mixture of hypochlorous acid and mercuric oxide, the latter being added by successive portions when required, and the liquid, after being filtered or mixed with a sufficient quantity of hydrochloric acid to dissolve all the mercuric oxide, is distilled, the first portion of the distillate passes over in oily drops, after which the distillation may be continued as long as the liquid which passes over becomes turbid on addition of potassium cyanide. Both these distillates contain a hydrate of monochloraldehyde, which solidifies when pure; it is most easily obtained from the second distillate. This liquid is saturated with sodium sulphate, and agitated with ether; the ether is distilled off from the ethereal extracts; the residuo is fractionally distilled, the portions going over between  $85^\circ$  and  $95^\circ-100^\circ$ , being collected apart; and both these distillates are dehydrated by suspending lumps of calcium chloride over them; whereupon, the hydrate of chloraldehyde separates in the solid state. Both this hydrate and the liquid decanted from it exhibit similar phenomena when rectified, the greater part distilling over between  $85^\circ$  and  $95^\circ$ , the smaller portion between  $95^\circ$  and  $100^\circ$ ; the former solidifies on cooling; the latter remains liquid for the most part, as also does the small residuo which boils above  $100^\circ$ .

The hydrate of chloraldehyde has the composition  $2C^2H^2ClO.H^2O$ . By evaporation of its ethereal solution, it is obtained in groups of flat tabular crystals, which melt at  $74^\circ-75^\circ$ . When exposed to the air it volatilises and oxidises at the same time. In dilute solution it smells like rotten apples or grapes, but its concentrated solutions have a pungent odour and give off a vapour which attacks the mucous membranes. It has a sweetish-sharp taste, and, when placed on the skin, produces spots which give no pain, and are scarcely visible at first, but afterwards become orange-yellow, and remain till the cuticle peels off. The hydrate reduces ammoniacal silver solution, producing a specular deposit. Sulphuric acid quickly converts it into a thick brown-yellow oil. With potassium cyanide it forms an oil which is converted by acids into chlorolactic acid (See LACTIC ACID). It unites with acid sodium sulphite, forming the compound  $2(C^2H^2ClO.NaHSO^3).H^2O$ ; which separates from the solution in boiling alcohol, as a bulky, white, crystalline powder.

The products of higher boiling-point obtained in the preparation of the hydrate, appear to contain nothing but condensation-products of chloraldehyde. The portion boiling between  $95^\circ$  and  $100^\circ$ , dissolves for the most part in water, and the insoluble portion gives, by analysis, a quantity of chlorine agreeing approximately with the formula  $2C^2H^2ClO - H^2O$ . The higher the boiling-points of these secondary products the less soluble are they in water; the aqueous solution of the higher-boiling products does not yield any oil with potassium cyanide. They all have a pungent

odour, a sweetish, burning taste, and do not combine with acid sodium sulphite. That these oily secondary products are formed from the solid hydrate of chloraldehyde appears from the fact; that, on distilling the perfectly desiccated hydrate, a portion boiling at 85°–90° and another at 90°–94° were obtained, both of which quickly solidified, but were no longer perfectly soluble in water; insoluble, oily drops remaining, which exhibited the properties above described. It does not appear possible to obtain anhydrous monochloraldehyde by continued distillations; a product thus obtained contained but little more chlorine (41.59 p.c.) than the hydrate (40.57 p.c.).

**Sulphaldehyde.**—When hydrogen sulphide is passed into an aqueous solution of aldehyde, an oil is formed, which, when treated with acids, yields a solid substance having the composition of aldehyde with the oxygen replaced by sulphur. Hofmann, however, finds that its vapour-density agrees with the triple formula  $(C^2H^2S^3)$ ; it is very easily formed from paraldehyde (*Zeitschr. f. Chem.* [2] vi. 699).

The oil formed by the action of hydrogen sulphide on aldehyde, was said by Weidenbusch (i. 107) to have the composition  $6C^2H^4S_3 \cdot II^2S$ , and to give off hydrogen sulphide when treated with acids. According to Pinner, however (*Deut. Chem. Ges. Ber.* iv. 257), these statements are incorrect. The oil is a compound of aldehyde and sulphaldehyde,  $C^2H^4O \cdot C^2H^2S$ , and when treated with an acid, yields a precipitate of sulphaldehyde  $C^2H^2S^3$ , and a solution of aldehyde, without any evolution of hydrogen sulphide. By passing sulphydric acid-gas through the strongly acid filtrate, a large quantity of sulphaldehyde may be directly obtained. In like manner, a strongly-acidulated solution of aldehyde yields, with sulphydric acid, not the oil above mentioned, but solid sulphaldehyde.

The oil,  $C^2H^4O \cdot C^2H^2S$ , solidifies at  $-8^\circ$  and liquefies again at  $-2^\circ$ . Its vapour-density was found to be between 61.3 and 59.4 ( $II=1$ ). Now, supposing that the oil is resolved by heat into monomolecular aldehyde  $C^2H^4O$  and trimolecular sulphaldehyde  $C^2H^2S^3$ , its vapour-density should be 61.2°, which agrees with the experimental number (Pinner).

**ALDEHYDE-ALCOHOLATE.**  $C^2H^4O \cdot C^2H^4O$ .—A compound identical with hydroxyl-ethyl-oxide (See ETHYL OXIDE).

**ALDEHYDE-ETHYL-CHLORIDE.**  $C^2H^4O \cdot C^2H^5Cl$ .—Identical with monochloroethyl oxide (See ETHYL OXIDE).

**ALDEHYDES.** *Reactions with Phenols.*—Acetic aldehyde, mixed with pyrogallol and hydrochloric acid, and gently warmed, produces a red coloration, becoming violet on the addition of an alkali. Bitter almond oil, heated with pyrogallol, produces a colourless body, crystallisable from ether, and having, when dried at  $120^\circ$ , the composition:  $C^{20}H^{22}O^7 = 2C^2H^4O + 2C^2H^2O^3 - H^2O$ . Heated to  $200^\circ$ , this product loses hydrogen, forming a red body,  $C^{20}H^{18}O^7$  soluble in alcohol, while, on treating it with hydrochloric acid, alcohol, and zinc, hydrogen is added, and a crystalline white body,  $C^{20}H^{20}O^7$ , is formed, soluble in acetone, but insoluble in alcohol and ether. Resorcin behaves with bitter almond oil in a similar manner to pyrogallol; and a phenol dyestuff is produced on adding strong sulphuric acid to a mixture of phenol and bitter almond oil. Aldehyde or chloral with phenol and sulphuric acid; furfural with resorcin, phenol, or pyrogallol and a trace of hydrochloric acid; salicylic and pyrotartaric acids with phenols: all give colouring matters (*A. Bayer, Deut. Chem. Ges. Ber.* v. 25).

*Condensation-products of Aldehydes (Aldanes, p. 32).*—Many aldehydes when treated with sodium yield condensation-products, with elimination of water. Thus, valeral  $C^5H^{10}O$ , yields an aldehyde,  $C^{10}H^{18}O = 2C^5H^{10}O - H^2O$ , which boils at  $195^\circ$ , combines with sodium bisulphite, and is converted by oxidation into an acid,  $C^{10}H^{18}O_2$ , and by nascent hydrogen into the alcohol  $C^{10}H^{22}O$ .

Enanthol, similarly treated, is converted into two polymeric modifications: one a liquid, the other a crystalline solid, both of which, on distillation, yield enanthol and condensation-products, with abstraction of water (*Borodin, Deut. Chem. Ges. Ber.* v. 480).

On the Thermal Effects of the Combination of Aldehydes with Bases, see HEAT.

**ALDEHYDINE.**  $C^4H^{11}N$ .—This base, discovered by Ador a. Bayer (*1st Suppl.* 82), is regarded by them as a homologue of picoline,  $C^4H^7N$ .—It is produced directly from Schiff's tetraldine, which again is formed by the union of 2 mol. crotonic aldehyde with ammonia (*Jahresb. f. Chem.* 1869, 707).

**ALDOL.**  $C^3H^6O^2 = CH^2-CHOH-CH^2-CHO$  (Wurtz, *Compt. rend.* lxxiv. 1361; lxxvi. 1166). A compound polymeric with acetic aldehyde, and regarded by

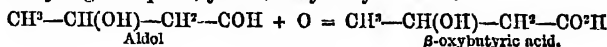
Wurtz as belonging to a class of bodies intermediate in properties and constitution between the aldehydes and the alcohols. It is formed by the action of hydrochloric acid and water on aldehyde at low temperatures: 1 part of aldehyde is mixed with 1 part of water and 2 parts of hydrochloric acid, and the mixture is left to itself for several days at a temperature of  $15^{\circ}$  to  $20^{\circ}$ ; in winter it must be placed in a stove. As soon as it has acquired a tawny colour, and smells but slightly of aldehyde and paraldehyde, it must be neutralised with crystals of sodium carbonate, and agitated several times with ether. The ethereal solution distilled in the water-bath leaves a transparent, slightly-coloured liquid, which becomes syrupy on cooling; and this product, distilled in a vacuum, gives off, first ether, then water, then between  $90^{\circ}$  and  $105^{\circ}$ , under a pressure of 2 centimeters, aldol, in the form of a colourless liquid, which remains soluble while hot and even when recently cooled, but when left to itself gradually becomes viscid, giving out, at the same time, a considerable quantity of heat. Thus a quantity of freshly-distilled aldol, perfectly limpid at  $11^{\circ}$ , gradually rose in an hour to the temperature of  $54^{\circ}$ , after which it slowly cooled, till, at the end of three hours more, its temperature was  $30^{\circ}$ : it was then viscid. This viscid aldol probably bears the same relation to mobile aldol that paraldehyde bears to ordinary aldehydes, the polymeric grouping being, however, less stable than that of paraldehyde.

Aldol at  $0^{\circ}$  is so viscid that it does not run out when the tube containing it is inverted. Its specific gravity is 1.208 at  $0^{\circ}$ , 1.1094 at  $16^{\circ}$ , and 1.0819 at  $49.6^{\circ}$ . It is strongly refractive, its index of refraction being 1.468 for the yellow ray, and 1.455 for the red. It has an aromatic and bitter taste, mixes in all proportions with water and alcohol, dissolves also in ether; when pure, it forms a clear solution with water.

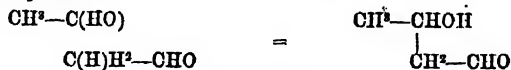
Aldol bears a heat of  $100^{\circ}$  without sensible alteration, and distils undecomposed at  $90^{\circ}$ , under a pressure of 2 centimeters; but, when heated above  $100^{\circ}$ , under the ordinary pressure, it begins to decompose at  $135^{\circ}$  into water and crotonic aldehyde ( $C^4H^6O^2 = H^2O + C^4H^4O$ ), and at  $150^{\circ}$  nothing remains in the vessel but a small quantity of viscid liquid. The same decomposition takes place when aldol is heated with glacial acetic acid. The formation of crotonic aldehyde by the action of hydrochloric acid on ordinary aldehyde (p. 34) is probably preceded by that of aldol.

Aldol possesses the reducing powers of the aldehydes; it throws down cuprous oxide from a cupric-potassic solution, and reduces ammoniacal silver nitrate, forming a fine silver speculum.

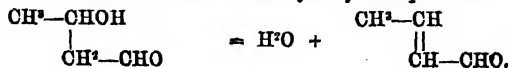
Nitric acid attacks aldol with great violence, giving rise to acetic aldehyde, oxalic acid, and several other acids not yet examined. Chromic acid likewise exerts a violent oxidising action. The action of silver oxide, on the other hand, is more moderate. When 1 mol. aldol is treated with 2 mol. moist silver oxide, the mixture becomes hot, and metallic silver is deposited. If the liquid be then boiled, filtered and concentrated, a silver salt separates out in long interlaced needles; which, when recomposed with hydrogen sulphide, yields  $\beta$ -oxybutyric acid.



Aldol therefore, as pointed out by Kolbe (*J. pr. Chem.* [2] v. 451), is the aldehyde of  $\beta$ -oxybutyric acid. Its formation from two molecules of acetic aldehyde is represented by this equation:

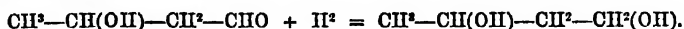


and its resolution into water and crotonic aldehyde by the equation:



By nascent hydrogen aldol is converted into one of the modifications of butylene-glycol,  $C^4H^{10}O^2$ . A 4 p. c. aqueous solution of aldol is heated at  $0^{\circ}$  with sodium-amalgam containing 6 p. c. sodium, the soda formed being continually neutralised with hydrochloric acid. The reaction is very slow, and the liquid must be decanted every evening, as otherwise it might become alkaline during the night, and the experiment would then be lost in consequence of the formation of resinous substances and condensation-products. As soon as the absorption of hydrogen ceases, the liquid is to be shaken several times with ether, which removes condensation-products soluble in water, the ethereal solution separated, and the remaining liquid evaporated at  $40^{\circ}$ . The residue is treated with alcohol, which leaves the greater part of the sodium chloride undissolved; the alcoholic solution is evaporated, and the residue treated with absolute alcohol, which separates a further quantity of sodium chloride.

The alcohol is then distilled off, and the remaining liquid, which distils between 200° and 220°, yields, by rectification, a thick saccharine liquid, boiling at 201°-203°, identical with the butylone-glycol which Kekulé obtained as a secondary product in the hydrogenation of aldehyde (p. 36). The formation of this glycol from aldol is represented by the equation:

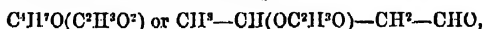


When a current of ammonia gas is passed into an ethereal solution of aldol, a syrupy colourless body is precipitated, which dries in a vacuum to an amorphous transparent, semi-resinous mass, consisting of ammonium-aldol,  $\text{C}^4\text{H}^7(\text{NH}^4)\text{O}^2$ . This compound is very soluble in water, and has an odour resembling that of aldehyde-ammonia.

When a current of hydrochloric acid gas is passed at 10° to the bottom of a concentrated aqueous solution of aldol, the aldol turns yellow and a thick liquid is deposited, insoluble in water, and probably containing monochloraldol ( $\text{CH}^2-\text{CHCl}-\text{CH}^2-\text{CHO}$ ).

Hydriodic acid produces with aldol a thick, yellow, unstable liquid. Phosphorus pentachloride acts very strongly on aldol, forming phosphorus oxychloride and a chlorinated body, probably having the composition  $\text{C}^4\text{H}^3\text{Cl}^2$ .

Aldol, heated for several days in the water-bath with 3 times its weight of acetic anhydride, combines with it, and water added to the product throws down an oily body, which, when distilled immediately under reduced pressure, is resolved into two acetates, one boiling under a pressure of 2 centimeters at 160°-100°, the other at 150°-160°. The former, which has the composition:



is a viscid, colourless, sensibly neutral liquid, insoluble in water, soluble in alcohol, decomposed by water at 100°, with formation of acetic acid, and resolved by baryta-water at the same temperature into acetic acid and yellow flocks, probably consisting of aldehyde-resin. The second acetate, which distils *in vacuo* at 150°-160°, has the composition  $\text{C}^4\text{H}^3(\text{C}^2\text{H}^3\text{O}^2)^2$ , and may be regarded as the diacetate of crotonic aldehyde; it is a thick, yellowish liquid, which stains paper like a fixed oil, but not permanently; is insoluble in water, and gives up acetic acid to that liquid when boiled with it. Saponified with baryta-water, it yields the resinous body above mentioned and 2 molecules of acetic acid.

Anhydride of Aldol,  $\text{C}^4\text{H}^{10}\text{O}^2 = (\text{C}^4\text{H}^7\text{O})^2\text{O} = 2\text{C}^4\text{H}^7\text{O}^2 - \text{H}^2\text{O}$ .—If the liquid obtained by heating aldehyde with water and hydrochloric acid, as above described, be allowed to stand till it acquires a brown tint and opaline appearance, and be then neutralised and treated with ether as before, the ethereal solution leaves saccharine scales which may be separated from the mother-liquid by means of Bunson's vacuum filter. The product thus obtained is the anhydride of aldol, and is probably related to aldol in the same manner as ether to alcohol. It distils at 137° under a pressure of 2 centimeters, forming a colourless, very viscid liquid, soluble in alcohol and ether, slightly soluble in cold water, more soluble in boiling water, which on cooling deposits it in crystals melting at 155°. It easily reduces ammoniacal silver nitrate and Fehling's cupric-potassic solution.

Aldol also loses water when heated for several hours to 60° in a current of dry air; it then thickens and solidifies on cooling to a colourless, transparent, viscid mass, insoluble in water.

Aldol, by its reducing power and by the readiness with which it unites with acids, exhibits considerable resemblance to the sugars. The aldehydes may, indeed, play an important part in the formation of glucose and similar bodies in the vegetable organism. The simplest of the aldehydes, namely, formic aldehyde,  $\text{H}.\text{CHO}$ , may possibly be formed in the processes of vegetation by the partial reduction of a molecule of water and a molecule of carbon dioxide:  $\text{CO}^2 + \text{H}^2\text{O} - \text{O}^2 = \text{CH}^2\text{O}$ ; and the condensation of several molecules of formic aldehyde may give rise to carbohydrates in the same manner as aldol is produced by the condensation of two molecules of acetic aldehyde. The condensation of two molecules of formic aldehyde would yield the first aldehyde of glycol,  $\text{CH}^2-\text{OH}-\text{CHO}$ , which is isomeric with glucose.

Benzoin  $\text{C}^8\text{H}^{10}\text{O}^2$ , is formed by the condensation of two molecules of benzoic aldehyde, just as aldol by that of two molecules of acetic aldehyde. If the two reactions are similar, the constitution of benzoin may be represented by the formula  $\text{C}^6\text{H}^4-\text{CHOH}-\text{C}^6\text{H}^4-\text{CHO}$ .

Borodin (*Deut. Chem. Ges. Ber.* v. 480) by treating acetic aldehyde with hydrochloric acid obtained a compound resembling Wurtz's aldol, but yielding by distillation chiefly acetic aldehyde, instead of water and crotonic aldehyde.

**ALIZARIN.** *Preparation.*—For the preparation of pure madder alizarin, the following process is recommended by Wartha (*Deut. Chem. Ges. Ber.* iii. 545, 673). Stuffs dyed with Turkey red are exhausted at the heat of the water-bath; with hydrochloric acid and alcohol; the solution is precipitated with potash; and the precipitate is decomposed with dilute hydrochloric acid and sublimed. Or the stuffs, after being freed from fatty matter by ligroin (light petroleum oil) may be exhausted with alcohol and hydrochloric acid, and the colouring matter precipitated by water. Pure alizarin may also be obtained by macerating the stuffs for two or three minutes in strong sulphuric acid, precipitating with water, and treating the precipitate with potash.

Madder alizarin sublimes between  $130^{\circ}$  and  $140^{\circ}$ ; artificial alizarin between  $280^{\circ}$  and  $300^{\circ}$ . For the sublimation of alizarin (and of anthracone), Wartha recommends the use of a wide glass tube exhausted by a mercury or water pump.

The peculiar fiery colour of fabrics dyed with Turkey red is attributed by Wartha to a peculiar fatty acid compound of alizarin, which may be extracted with ligroin and ether.

With reference to Wartha's observations, Bolley (*Dingl. polyt. J.* xcvi. 357) remarks that the methods of separating madder colours from dyed fabrics were described long ago by himself and others.

*Isalizarin*  $C^{14}H^{10}O^4$  (Rochleder, *Deut. Chem. Ges. Ber.* iii. 292; *Zeitschr. f. Chem.* [2] vi. 573).—Madder which has been heated with mineral acids, contains, besides alizarin and purpurin, certain yellow crystallised substances which are, perhaps, present in the root in the form of glucosides. Their quantity is small, many thousand pounds of madder being required to yield a few ounces of them. The material, a waste product of a manufacturing operation, was obtained in the form of yellow, hard, light, easily pulverisable lumps. It dissolves with red colour, in caustic soda; and the solution, treated with hydrochloric acid, deposits dirty-yellow gelatinous flocks, which shrink and lose their gelatinous character when boiled with water, so that they can then be easily washed on a filter. The substance thus obtained dissolves in baryta-water, a nearly black powder remaining behind. The blood-coloured solution, neutralised with hydrochloric acid, yields a yellowish precipitate, which dissolves when boiled with glacial acetic acid, forming a reddish-yellow solution, which, if the quantity of acetic acid used was only just sufficient to dissolve the precipitate, solidifies on cooling to a cake of small crystals, which must be washed on a filter with glacial acetic acid as long as the liquid which runs through exhibits the colour of a saturated solution of potassium dichromate. By this treatment an amorphous resinous body, easily soluble in cold acetic acid, is removed, while only a small quantity of the other constituents passes into solution. The lemon-yellow mass remaining on the filter is separated into its constituents by fractional crystallisation, first from dilute acetic acid, then from hot alcohol, partial solution in alcohol, and partial precipitation of the alcoholic solutions with water.

The compound which is present in largest quantity in the mixture, after removal of the resinous body above mentioned, is isalizarin, a body having the same composition as alizarin, but distinguished from it by the blood-red colour of its solutions in caustic potash and soda, and the red colour of its solution in baryta-water. In the solid state it has a colour nearly intermediate between that of alizarin and that of purpurin. It does not dye calico mordanted with iron or alumina.

The isalizarin is accompanied by small quantities of three other bodies, viz.:  $\alpha$ . A body bearing a very close resemblance to isalizarin, and having the composition  $C^{14}H^{10}O^4$ .  $\beta$ . *Hydrisalizarin*  $C^{22}H^{18}O^6$ , which has a somewhat lighter yellow colour than isalizarin, dissolves with dark brown colour in a boiling solution of ferric chloride, and separates therefrom partly on cooling, partly on addition of a few drops of hydrochloric acid, in light yellow flocks, which exhibit the same composition.  $\gamma$ . A body,  $C^{22}H^{20}O^6$ , which, when heated for a long time to  $118^{\circ}$ – $120^{\circ}$ , gives off a molecule of water and assumes a darker colour.

*Distinction between Alizarin and Purpurin.*—When cloth dyed or printed with madder is boiled for a short time with a strong solution of aluminium sulphate, a liquid is obtained which appears red with a bluish tinge by transmitted light and exhibits a gold-green iridescence by reflected light. This appearance is due to purpurin. A solution of alizarin exhibits slight fluorescence only when a beam of light is thrown into it by a lens. Alizarin separates from the solution in aluminium sulphate in the course of twelve hours; purpurin does not. A solution of aluminium sulphate serves in this manner to detect the presence of purpurin and therefore of madder-colour. Alizarin may be detected, in presence of purpurin, by repeatedly boiling the red colour with potassium carbonate, which dissolves the compound of alumina and purpurin. If the colour does not afterwards appear bleached, the presence of alizarin may be



inferred; in that case also the colour is turned violet by immersion in baryta-water (W. Stein, *Zeitschr. f. Chem.* vi. 479)."

**Artificial Alizarin.**—The following method of preparing alizarin from anthracene paranaphthalene and their homologues is given by A. Girard (*Bull. Soc. ind. de Mulhouse*, xliii. 54; *Dingl. polyt. J.* ccciv. 490). The material used is that which distils between 290° and 360°; it is purified by distillation and pressure, the portion which passes over between 300° and 335° being collected apart. This mixture is treated with potassium chlorate and hydrochloric acid, whereby it is converted into tetrachlorinated products. These are oxidised either by nitric acid in the water-bath, or by a metallic oxide (red or brown oxide of lead), and sulphuric or acetic acid. In the first case, a mixture of dichloranthraquinone and chloride of chloroxyanthranil are obtained. These substances are treated, in presence of a metallic oxide (zinc oxide, cupric oxide, or litharge), with an alcoholic solution of sodium acetate. The metallic oxide removes the last atom of chlorine from the sodium chloroxyanthranilate, and converts it, like the dichloranthraquinone, into alizarin.

The purification is effected by means of benzene, petroleum, &c., which dissolve out the foreign matters, and by successive precipitation from the alkaline solutions by mineral acids. The foreign matters may also be separated by means of a little alum, when it is necessary to work with neutral potash or soda salts.

The following method has been patented by Dale & Schorlemmer (*Deut. Chem. Ges. Ber.* iii. 838):—1 pt. of anthracene is boiled with 4 to 10 pts. of strong sulphuric acid, then diluted with water, and the solution neutralised with carbonate of calcium, barium, potassium or sodium. The resulting sulphates having been removed by filtration or crystallisation, the solution is heated to 180°–260° with caustic potash or soda, to which a quantity of potassium nitrate or chlorate has been added, about equal in weight to the anthracene—as long as a blue-violet colour is thereby produced. From this product the alizarin is separated in the usual way by precipitation with acid.

On Artificial Alizarin, see also *Deut. Chem. Ges. Ber.* iv. 978; *Chem. Soc. J.* [2] x. 621, 622.

On a secondary colouring matter produced in the manufacture of Alizarin from Anthracene, see ANTHRAPHURPURIN.

**Red Colour-printing with Artificial Alizarin.**—A. Müller (*Chem. Centralblatt*, 1871, 304) obtains a red, similar in tint and purity to Turkey red, from anthracene-alizarin by a process of direct printing.

The pigment (containing much anthrapurpurin) in a pasty form, and having 25 p.c. of dry material, is dissolved in boiling spirit in the proportion of 1 : 5, and immediately mixed with a concentrated solution of aluminium chloride of which the pure  $AlCl_3$  is to the weight of the colouring matter as 1 : 3. The liquid is thickened with a little tragacanth, and for every half litre of this mixture, 30 c. c. of a solution of the best olive-oil in sulphuric acid and a little spirit (15 : 1 : 15) is stirred in. This solution must be as thin as possible, but thick enough to withstand the capillarity of the cloth. The cotton cloth with which this colour is to be used is first impregnated with a solution of aluminium acetate of about 8° B., and after drying and two days' airing, is passed through a soap-bath containing 30 grams of Marseilles soap to the litre of water, then well washed out and dried.

The cloth printed with the above mixture is now exposed to strongly ammoniacal steam at a moderately high pressure, passed through a weak soap-bath, washed in a stream, and passed through the following series of liquids:—1. Cold nitric acid, 3 c. c. to 1 litre water. 2. Washed in stream. 3. Cold nitric acid, 5 c. c. to 1 litre water. 4. Tin salt,  $\frac{1}{2}$  gram tin salt to 1 litre water at 30° C. 5. Washed in stream. 6. Liquor of Javelle, 15 c. c. of 8° B. to 1 litre water, cold. 7. Thorough washing. The colour is now thoroughly developed, and behaves to light, air, and soap like ordinary Turkey red. In preparing the aluminium chloride (by addition of barium chloride to aluminium sulphate) it is absolutely necessary to avoid an excess of the barium salt.

**Bromalizarin**,  $C^{14}H^7BrO^4$ , is formed by heating alizarin and bromine together with carbon sulphide to 170°; in the dry state the two substances do not act upon each other. By crystallisation from glacial acetic acid, the bromalizarin is obtained in orange-red needles; it dissolves in caustic alkalis with a blue-violet colour, similar to that obtained with alizarin, and giving a similar absorption-spectrum. Bromalizarin dyes a redder violet with iron mordants, and a browner red with alumina mordants than alizarin (Perkin, *Chemical News*, xxvii. 317).

**Diacetyl-alizarin**,  $C^{16}H^{12}O^6 = C^{14}H^7O^4 \begin{Bmatrix} OC^2H^3O \\ OC^2H^3O \end{Bmatrix}$ , isomeric with diacetyl-anthraflavic acid, is formed by heating alizarin with acetic anhydride for some hours to 180° in a sealed tube. It separates on cooling as a yellow crystalline substance, which may be purified by heating it with water, drying, and recrystallising two or three times

from alcohol. It is then obtained as a pale yellow substance, crystallising in flat needles or plates. It melts at  $160^{\circ}$ , or  $68^{\circ}$  lower than diacetyl-anthraflavic acid, and is much more soluble than the latter in alcohol and in glacial acetic acid. By heating with alcoholic potash, it is decomposed, with formation of potassium alizarate (Perkin, *Chem. Soc. J.* [2] xi. 21).

When diacetyl-alizarin is added gradually and in small quantities to nitric acid of sp. gr. 1.5, a solution is formed, which, on being slowly added to a large quantity of cold water, deposits a precipitate which dissolves in glacial acetic acid, and crystallises therefrom in needles. This substance dyes alumina mordants a bright orange colour, and iron mordants of a very red purple. The colours are superior to those produced by the nitro-derivative obtained in like manner from anthrapurpurin. It dissolves in alkalis with a purple colour, and the solution gives a spectrum showing a considerable absorption in the orange, which appears to consist of two indistinct bands. It does not appear to be identical with the nitroxyalizarin obtained by Strecker (*Bull. Soc. Chim.* [2] xi. 260), as that substance forms red solutions with alkalis (Perkin, *Chem. Soc. J.* [2] xi. 430).

*Methyl-alizarin*,  $C^{12}H^{10}O^1 = C^{14}H^4(OH)(OCH^3)^2O^2$ .—This compound may be prepared by treating artificial alizarin with a mixture of methyl iodide, caustic potash, and a little methyl alcohol in closed tubes, at a moderate temperature, evaporating the contents of the tubes to dryness, and treating the residue successively with water, alcohol, and dilute caustic potash. The second residue, which was found to consist mainly of the potassium compound of methyl-alizarin,  $C^{14}H^4(OK)(OCH^3)^2O^2$ , is treated with hydrochloric acid, and the insoluble orange-coloured flocks dissolved in boiling alcohol. The alcohol, on cooling, deposits crystalline needles of methyl alizarin.

Methyl-alizarin crystallises in long reddish-yellow needles, which are almost insoluble in boiling water, but readily soluble in oil of vitrol. It volatilises entirely by heat, yielding a sublimate of lustrous yellow scales. It dissolves without decomposition in a boiling solution of caustic potash, but when carefully fused with that alkali, it is converted into alizarin. It differs essentially from alizarin in the appearance of its spectrum, its solution in caustic potash showing no trace of absorption-bands, but only a general obscuration of the green part of the spectrum. The solution in strong sulphuric acid, however, shows an absorption-band between the green and the blue, similar to, but less distinct than that exhibited by a solution of anthraflavic acid. It differs also from alizarin in not being capable of dyeing mordanted cloth, while it resembles anthraflavic acid in its capability of forming crystallisable potassium and sodium compounds (Schunck, *Chemical News*, xxvii. 171).

**ALIZARIN-SULPHONIC ACID.** Alizarin heated with fuming sulphuric acid forms a sulfo-acid, whose salts are about as soluble as the corresponding sulphates. When fused with potash it yields alizarin.

**ALKALIS.** On Alkanna-red as a test for Alkalis, see **ALKANNA**.

Respecting the determination of Alkalis in silicates, see **SILICATES**.  
On the heat evolved in the electrolysis of Alkaline Bases, see **HEAT**.

**ALKALOIDS.** Bourgoïn (*Bull. Soc. Chim.* [2] xii. 438) has examined the action of the electric current on the neutral and acid sulphates of atropine, brucine, codeine, quinine, and strychnine, with the following results:—

1. The current decomposes the salts of organic bases in the same manner as inorganic salts—that is to say, the basic element goes to the negative pole, while the remaining constituents of the salt are eliminated at the positive pole.
2. In an acid, and also, though less easily, in a neutral solution, the same colour is produced by the action of the current as by addition of nitric acid, whence it follows that those colours are quite independent of the production of a nitro-compound.
3. The gas evolved at the positive pole does not consist entirely of oxygen, but contains also carbon monoxide and dioxide, sometimes in equal volumes.
4. Besides these gases, various products are formed, chiefly compound ammonias, formed by decomposition of the alkaloids under the influence of oxygen, which produces a gradual combustion, more energetic as the solution is more acid.

*Reaction of Alkaloids with Sugar and Sulphuric acid.*—*Morphine* is at once coloured a beautiful purple-red, when a small quantity of the mixture of the base (or its salts) with 6 or 8 pts. of sugar is treated with concentrated sulphuric acid. No browning of the sugar is observed. The colour lasts from  $\frac{1}{2}$ –1 hour, then gradually becomes blue, violet, dirty blue-green, and lastly, dirty-yellow. This series of colours can be rapidly produced by adding a little water. 0.00001 gram can be clearly indicated by this reaction. Dilute solutions of morphine are to have about as much sugar added as will dissolve in them, and then to be brought in contact with sulphuric acid, when a beautiful rose-red zone will develop itself where the two liquids meet.

**Codeine** closely resembles morphine, except that the reaction succeeds best when the sulphuric acid is not the most concentrated. Codeine is distinguished from morphine by being readily taken up by chloroform from an alkaline solution.

**Aconitine** is coloured a beautiful rose-red, soon becoming dirty violet and brown. The aconitine is to be stirred with a drop of sulphuric acid, and then a drop of concentrated sugar-solution brought in contact with it. There is a certain degree of resemblance between the reactions of aconitine and those of morphine and codeine. It is distinguished, however, from them by Dragendorff's process for separating the alkaloids; codeine and aconitine are taken up by benzene from an alkaline solution, but not morphine; aconitine is quite insoluble in water; codeine dissolves easily, especially in hot water.

**Delphinine**, intimately mixed with a drop of sugar-solution on a porcelain plate, gives also a characteristic reaction, when a small drop of sulphuric acid is dropped into the middle of it. The acid becomes yellow, then yellowish-brown with a dirty-green border, and on addition of a small drop of water, assumes a magnificent green colour, which soon passes into a dirty green, and then into brown.

The behaviour of *narcotine*, *narceine*, *cinchona-bases*, *strychnine*, *brucine*, *atropine*, *colchicine*, *emetine*, and *picrotoxine* is not characteristic (R. Schneider, *Pogg. Ann.* cxlvii. 128).

**Reactions with Ceroso-ceric oxide.**—This oxide exhibits characteristic colours with several alkaloids, especially with *strychnine*. When strong sulphuric acid is poured upon strychnine, and then a small quantity of ceroso-ceric oxide added, a fine blue colour is produced, similar to that which strychnine exhibits with potassium bichromate, but much more permanent. The blue colour gradually changes to cherry-red, and then remains unaltered for several days. This reaction is capable of detecting 1 pt. of strychnine in a million pts. of liquid. *Brucine*, similarly treated, acquires an orange-colour gradually changing to yellow; *morphine*, olive-brown, finally brown; *narcotine*, brown cherry-red, finally wine-red; *codeine*, olive-green, finally brown; *quinine*, pale-yellow; *cinchonine* and *theine* remain colourless; *veratrine* becomes reddish-brown; *atropine*, dingy yellowish-brown; *solanine*, yellow at first, finally brownish; *emetine*, brown; *colchicine*, first green, then dirty-brown; *aniline*, after a long time, acquires a blue colour extending from the edges inwards; *conine* becomes light-yellow. *Piperine* colours the sulphuric acid blood-red, and is turned dark-brown, almost black, by the cerium oxide (Sommerschein, *Deut. Chem. Ges. Ber.* iii. 632).

**Reaction with Cyanides.**—According to Flückiger (*Chem. Centr.* 1872, 741), the hydrocyanides of the alkaloids cannot be prepared by double decomposition with metallic cyanides or by the action of hydrocyanic acid on their alcoholic, aqueous, or alkaline solutions, the precipitates so formed consisting only of the pure bases.

**Reaction with Picric acid.**—According to Hager (*Zeitschr. Ann. Chem.* ix. 110), this acid is a very good precipitant for alkaloids, affording a very delicate test for many of them, and may, perhaps, also serve for separating them one from another. The precipitation takes place even in solutions containing a large excess of sulphuric acid, and is sometimes complete. *Precipitated* are: brucine, strychnine, veratrine, quinine, quindine, cinchonine, most of the opium alkaloids, aconitine (?); *not precipitated*: morphine, atropine (English); pseudo-morphine, caffeine, and all glucosides.

**Compounds of Alkaloids with Bile-acids.**—The gall of oxen, pigs, and dogs, and the sodium salts of glyco-, hyoglyco-, and tauro-cholic acids, give crystalline precipitates with some alkaloids, amorphous with others; the precipitates usually contain excess of acid, and are decomposed by diffusion, and dissolved by hydrochloric acid, re-appearing on neutralisation; excess of bile or bile-acids also dissolves them. The salts of strychnine, brucine, quinine, cinchonine, veratrine, emetine, and quindine give difficultly soluble compounds, while those of morphine, nicotine, and conine are easily soluble; the strychnine and quinine compounds are about as energetic physiologically as the nitrates and hydrochlorides of these bases respectively (W. F. de l'Arbre, *Chem. Centrbl.* 1872, 231).

**ALKANNA.** Böttger (*J. pr. Chem.* cvii. 146) recommends alkannin or alkannared as a very delicate test for alkalis, especially for ammonia. Strips of paper dyed red with alcoholic solution of alkannin are instantly turned blue, when moistened, by mere traces of ammonia. The same papers, turned blue by a dilute solution of sodium carbonate, serve for the detection of the smallest traces of free acid. The papers may be preserved unaltered for any length of time in glass vessels.

J. B. Enz (*Jahresb.* 1870, 935) prepares these red papers by exhausting dried alkanna root with about 4 parts of ether at ordinary temperatures, filtering, and dyeing strips of Swedish filter-paper with the splendid ruby-coloured solution.

**ALLOPETHRE.** See PEPTONES.

**ALLANIC ACID**,  $C_4H_5N_3O_5$ . (E. Mulder, *Ann. Ch. Pharm.* elix. 353).—An acid produced by the action of nitric acid on allantoin. It is best prepared by gradually

adding powdered allantoin to red fuming nitric acid in a well-cooled porcelain dish till the whole is dissolved. On leaving the solution to stand for some time, till a crystalline crust forms on the surface, and recrystallising this crust from water, allantoic acid is deposited in beautiful stellate groups of needles, consisting of a hydrate  $C^4H^4N^4O^5 \cdot H^2O$  isomeric with nitrate of allantoin  $C^4H^4N^4O^5 \cdot HNO^3$ .

Allantoic acid has an acid reaction, is sparingly soluble in cold water, and decomposes gradually when its aqueous solution is evaporated. The crystals give off their water gradually at ordinary temperatures, more quickly when heated in a test-tube to about  $90^\circ$ , becoming dull at the same time.

Allantoic acid decomposes at  $210^\circ$ – $220^\circ$  without fusion or evolution of red vapours. It chars when heated on platinum-foil. It does not bleach indigo-solution when mixed with hydrochloric acid, or give off gas with nitric acid containing nitrogen tetroxide. It does not give a precipitate with calcium chloride, even on addition of ammonia. It is precipitated by silver nitrate on addition of ammonia, and by basic lead acetate, but not by the neutral acetate.

Allantoic acid is monobasic. It dissolves readily in ammonia at ordinary temperatures, and the solution on standing deposits well-formed prisms of the ammonium salt  $C^4H^4(NH^4)^1N^4O^5$ . From the concentrated solution of this salt allantoic acid is precipitated in stellate needles of the hydrate above described. Allantoic acid decomposes potassium carbonate, and the solution, after a while, deposits prisms of potassium allantate. The silver salt is obtained on adding silver nitrate to ammonium allantate, as an amorphous precipitate, which dissolves in warm water, and is deposited on cooling in crystals having the composition  $C^4H^4AgN^4O^5 + H^2O$ : its ammoniacal solution is decomposed by exposure to light, and deposits metallic silver. It does not detonate, even when heated. The neutral lead salt,  $Pb(C^4H^4N^4O^5)^2 \cdot H^2O$ , is obtained by gradually adding neutral lead acetate to a saturated solution of allantoic acid, as a warty mass which does not lose weight at  $130^\circ$ . A basic lead salt is obtained by adding basic lead acetate to an excess of allantoic acid; after drying at  $100^\circ$  in a stream of dry air, it has the composition  $Pb(C^4H^4N^4O^5)^2 \cdot PbH^2O^2$ . Another basic salt, containing  $2Pb(C^4H^4N^4O^5)^2 \cdot 5PbH^2O^2$ , perhaps a mixture of  $Pb(C^4H^4N^4O^5)^2 \cdot 2PbH^2O^2$  and  $Pb(C^4H^4N^4O^5)^2 \cdot 3PbH^2O^2$ , is obtained by precipitating allantoic acid with excess of basic lead acetate, and drying the precipitate at  $100^\circ$  in a stream of air. The barium salt crystallises with difficulty; the magnesium salt apparently not at all.

Allantoic acid appears not to have the constitution of nitro-allantoin,  $C^4H^4(NO^2)N^4O^4$ , inasmuch as it is not reduced by hydrogen sulphide in a strongly ammoniacal solution; moreover, it is less easily reduced than allantoin by a strong solution of hydrogen iodide; and its silver salt is not explosive.

**ALLANTOIC ACID.**  $C^4H^4N^4O^5$  (E. Mulder, *Ann. Ch. Pharm.* cliz. 362).—An acid produced by addition of the elements of water to allantoin ( $C^4H^4N^4O^3 + H^2O$ ): it was obtained in an impure state by Schlieper, who called it *hydantoic acid* (iii. 177); that term, however, is now more appropriately applied to the acid  $C^4H^4N^4O^3$ , formed by hydration of hydantoin (1st Suppl. 702).

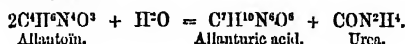
A solution of allantoin in aqueous potash which has stood for some days, no longer gives a precipitate with acetic acid even after some time; but if acetic acid be added to acid reaction, then a little alcohol, and the liquid be left in an exsiccator over lime, the potassium salt of allantoic acid,  $C^4H^4KN^4O^5$ , gradually separates in hard crusts, composed of stellate crystals, which, after recrystallisation, exhibit a neutral reaction. The solution of this salt gives crystalline precipitates with neutral lead acetate and silver nitrate; no precipitate with barium chloride till alcohol is added, whereupon a curdy and very hygroscopic precipitate is formed.

**ALLANTOIN.**  $C^4H^4N^4O^3$  (E. Mulder, *Ann. Ch. Pharm.* cliz. 349).—In preparing this compound by Liebig & Wöhler's method, namely, oxidation of uric acid with lead dioxide (i. 130), the yield is found to be increased by using about one litre of water to every 25 grams of uric acid, instead of the smaller quantity usually recommended. The greatest yield is obtained by effecting the decomposition at the ordinary temperature. 100 grams of uric acid are stirred up with 1 to 2 litres of water, a small quantity of acetic acid is added to start the reaction; the necessary quantity of lead dioxide is gradually introduced; and the mixture is exposed to bright daylight.

For 100 grams of uric acid the dioxide from 1.5 kilogram of red lead is required; both the dioxide and the uric acid are employed in the dried state. The decomposition being ended, the whole is heated and filtered, and the residue is repeatedly exhausted with warm water; the filtrates, to which a small quantity of acetic acid is added, are evaporated and filtered. On cooling, the allantoin separates out, and a further quantity is obtained on concentrating the mother-liquor. 100 grams of uric acid thus treated yield 30–32 grams of pure allantoin.



evaporating the solution, a sticky substance is left which solidifies on cooling to a hard transparent amorphous mass. This mass recrystallised from water gives stellate crystals of allanic acid, and on leaving the mother-liquor to stand in an exsiccator, a further quantity of allanic acid crystallises out, together with urea nitrate, gas being evolved at the same time. The syrupy residue having been repeatedly washed with cold water till no further deposition of crystals or evolution of gas took place, the solution was fractionally precipitated with basic lead acetate, whereby a series of precipitates was obtained, one of the later of which gave by analysis 10.6 p. c. nitrogen and 10.9 p. c. carbon (nearly equal quantities), and 17.1 p. c. lead. This is nearly the composition of the lead salt of an acid containing  $C^2H^{10}N^4O^4$ . Its formation may be represented by the equation:



Polouze assigned to this acid the formula  $C^2H^{11}N^4O^4$ , but his analysis gave less nitrogen than that required by this formula. Gerhardt (*Chimie organique*, i. 528) proposed the formula  $C^2H^4N^4O^4$ .

Allanturic acid is also formed, but apparently without allanic acid, by evaporation with hydrochloric acid. The lead salt of the resulting acid gave 10.8 p. c. carbon and 10.8 nitrogen. The quantity of allanturic acid obtained by either process is, however, very small.

**ALLOPHANE.** A specimen of this mineral from Dehn, near Limburg in Nassau, examined by G. vom Rath (*Pogg. Ann.* cxliv. 594), consists of a principal stalactite 8 centimeters long and about 4 thick, to which are attached a number of smaller ones from 5 to 10 mm. long. It is perfectly transparent and colourless; has a strong lustre inclining to fatty; a conchoidal fracture; and is very brittle. The analysis of the mineral dried at 25° and ignited, gave the following results:—

	LPO	AP <sup>2</sup> O <sup>3</sup>	CaO	H <sup>2</sup> O	
Ignited	37.28	59.76	3.05	—	= 100.09.
Dried at 25°	23.53	37.73	1.92	36.86	= 100.04.

reckoning the small quantity of lime as silicate,  $2CaO.SiO^2$ , those numbers lead to the formula  $Al^2O^3.SiO^2$ , or  $Al^2SiO^3$  for the anhydrous, and  $Al^2SiO^3.5H^2O$  for the hydrated mineral. About half the water is given off at 100°; nearly half the remainder by prolonged heating to 200°–220°; the rest at a red heat, but not quickly, except at the heat of a lamp urged by the blowpipe.

The specific gravity of the mineral in its natural state is 2.079; that of the ignited mineral 2.406.

**ALLOXAN** boiled with solution of sodium nitrate and a little acetic acid is converted into sodium oxalurate, which, by prolonged boiling, is resolved into oxalic acid and urea.

Barium alloxanate treated in the same manner yields not quite pure barium oxalate.

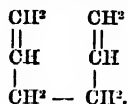
Alloxantin boiled with sodium nitrate and acetic acid is oxidised to alloxan (Gibbs, *Sill. Am. J.* [2] xlviii. 215).

**ALLYL**, or **DIALLYL**.  $C^3H^5 = C^2H^3.C^2H^2$ .—Wagner a. Tollens (*Deut. Chem. Ges. Ber.* vi. 588) obtained this hydrocarbon in attempting to prepare allyl-benzene by heating together 48 pts. of allyl bromide, 56 pts. bromobenzene, 102 pts. benzene, and 23 pts. sodium to 60°. An energetic action took place which had to be moderated by cooling; and by subsequently distilling the product over a naked flame, a liquid was obtained consisting principally of benzene and allyl, but not containing any allyl-benzene. In another experiment the distillation was effected over the water-bath, and the residue was treated with alcohol; the addition of water then caused the separation of an oily substance, which, on distillation in a current of steam, yielded a small portion of a distillate containing diallyl, but no allyl-benzene, and a thick residue smelling of cinnamon, which deposited crystals apparently consisting of diphenyl. Wagner a. Tollens think it probable that this thick oil, which combined with bromine, contained a polymeride of allyl-benzene.

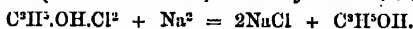
The diallyl formed as above yielded a *tetrabromide*,  $C^6H^{10}Br^4$ , which, after purification, melted at 62.5°–63.5°. Now this compound is generally said to melt at 37°. To reconcile this difference, diallyl was prepared:  $\alpha$ . By the action of sodium on a mixture of allyl bromide and benzene.  $\beta$ . By Oppenheim's method of treating mercuric iodallyl,  $C^2H^3HgI$ , with potassium cyanide (p. 51).  $\gamma$ . By the action of finely divided silver on allyl bromide. Diallyl from these several sources was found to boil

at 58°-60°, and its tetrabromide, after purification, melted at 60°-63·5°, agreeing, therefore, with that obtained by the first method.

The boiling point of diallyl appears to indicate that it is analogous in structure rather to di-isopropyl than to normal dipropyl, its constitutional formula being probably



**ALLYL ALCOHOL**,  $\text{C}^3\text{H}^5\text{O}$ , or  $\text{CH}^2=\text{CH}-\text{CH}^2\text{OH}$ , is formed by the action of sodium on dichlorhydrin (Hübner a. Müller, *Zeitschr. f. Chem.* vi. 344):



According to Tollens (*Ann. Ch. Pharm.* elviii. 104), pure allyl alcohol, carefully dehydrated with lime, boils at 96°-97°, a somewhat higher temperature than that previously given by the same chemist (*L. Suppl.* 9). Its specific gravity, determined at different temperatures, is as follows:

Temp.	Sp. gr.	Temp.	Sp. gr.
0° . . . . .	0·8079	62° . . . . .	0·81832
13° . . . . .	0·86045	75·5° . . . . .	0·80631
25° . . . . .	0·85074	87·5° . . . . .	0·79353
47·5° . . . . .	0·83107	93·5° . . . . .	0·78882

These numbers give for the expansion of allyl alcohol by heat, the following formula:—

$$V_t = V_0 + 0·000879t + 0·0000026t^2.$$

This gives, for the specific gravity of allyl alcohol at 97° compared with that of water at 0°, the number 0·7846, whence the specific volume is  $\frac{58}{0·7846} = 73·92$ , which

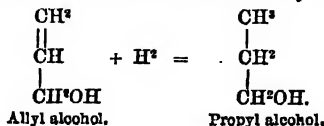
agrees well with the theoretical value calculated by Kopp, namely 73·8. Hence it may be inferred that the oxygen of allyl alcohol, which is present as hydroxyl, enters with the atomic volume 7·8; whereas the oxygen of the isomeric body acetone, which is present as CO, has the value 12·2\*.

The boiling point of allyl alcohol is the same as that of normal propyl alcohol; the boiling points of the chloride, bromide, iodide, formate, acetate, and other ethers of allyl have likewise been found by Tollens to agree with those of the corresponding normal propylic ethers. The agreement between the boiling points of the corresponding allyl and propyl compounds (except diallyl) may therefore be looked upon as general.

Allyl alcohol oxidised with chromic acid mixture gives off an odour of acrolein, and yields, on distillation, formic but no acetic acid (Rinne a. Tollens, *Zeitschr. f. Chem.* [2] vii. 250).

Allyl alcohol unites with *hypochlorous acid*, forming monochlorhydrin,  $\text{C}^3\text{H}^4(\text{OH})^2\text{Cl}$ ; the yield is however but small, as the greater part of the alcohol undergoes oxidation (L. Henry, *Deut. Chem. Ges. Ber.* v. 449).

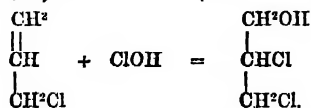
Allyl alcohol, heated with an equal weight of potassium hydrate to 105° in a flask with inverted condenser, takes up hydrogen and is partly converted into normal propyl alcohol, while ethyl alcohol, formic acid, and acrylic acid are obtained as secondary products. The formation of normal propyl alcohol by this reaction shows that allyl has the constitution  $\text{CH}^2=\text{CH}-\text{CH}^2\text{OH}$ , as indicated by the equation:



Another allyl alcohol is, however, possible, namely, that represented by the formula  $\begin{array}{c} \text{H}^2\text{C} \\ \diagdown \\ \text{H}^2\text{C} \end{array} \text{CHOH}$ . This is, perhaps, the isoallyl alcohol which Berthelot obtained by treating allylene with sulphuric acid, and distilling the product with water.

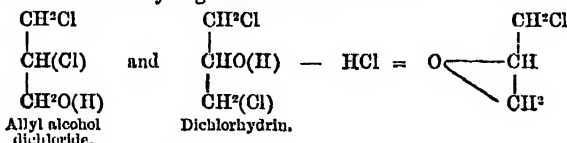
\* According to Buff (*Deut. Chem. Ges. Ber.* iv. 647), the above determination of the atomic volume of allyl alcohol is not quite exact.

The *dichloride of allyl alcohol*,  $C^3H^4OCl^2$ , which Tollens obtained by direct addition of chlorine to allyl alcohol (1st *Suppl.* 91), is likewise produced: a. By addition of hypochlorous acid to allyl chloride (v. Gegerfeldt, *Ann. Ch. Pharm.* cli. 247; *Deut. Chem. Ges. Ber.* vi. 720).



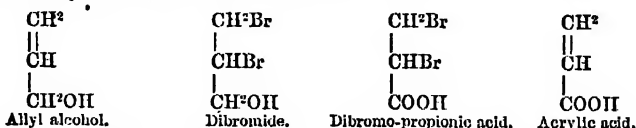
8. Together with the isomeric compound, dichlorhydrin,  $CH^2Cl-CHOH-CH^2Cl$ , by passing dry hydrochloric acid into a mixture of glycerin and glacial acetic acid. The two isomerides may be separated, though not completely, by fractional distillation, dichlorhydrin boiling at  $174^\circ$ , allyl alcohol dichloride at about  $182^\circ$ . The latter is best prepared by the action of dry chlorine on allyl alcohol dehydrated with lime (Hübner a. Müller, *Ann. Ch. Pharm.* cli. 168). It is a viscid oil, having a faint ethereal odour, and a specific gravity of 1.355 at  $17.5^\circ$ , soluble in alcohol and in a large quantity of water (v. Gegerfeldt).

Both dichlorhydrin and allyl alcohol dichloride, when treated with caustic soda-solution, which abstracts hydrochloric acid, yield one and the same epichlorhydrin, boiling at  $118^\circ-119^\circ$ . This is easily explained by the following equation, in which the eliminated chlorine and hydrogen atoms are bracketed:—



This transformation, therefore, does not enable us to decide which of the two isomerides is represented by the symmetrical, and which by the unsymmetrical formula; but the formation of allyl-alcohol dichloride by direct addition of chlorine to the alcohol leads to the conclusion that it has the constitution  $CH^2Cl-CHCl-CH^2OH$ , which is further corroborated by its analogy to the dibromide.

*Allyl-alcohol dibromide*,  $C^3H^4Br^2O$ , oxidised with chromic or nitric acid, is converted into dibromopropionic acid  $C^3H^3Br^2O^2$ , which, when treated with zinc-dust, is converted into acrylic acid  $C^3H^3O^2$ . This reaction leads to the conclusion that dibromide of allyl alcohol contains the group  $CH^2OH$ , and is represented by the formula  $CH^2Br-CHBr-CH^2OH$ , which is, moreover, in accordance with its formation from allyl alcohol by direct addition of bromine:—



(Tollens, *Zeitschr. f. Chem.* [2] vii. 305.)

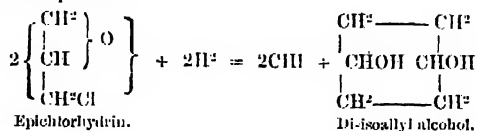
*Allyl-alcohol dicyanide*,  $C^3H^4(CN)^2O$  =  $C^3H^4(CN)^2OH$ , is obtained by passing cyanogen gas for some time into allyl alcohol, washing with salt water, drying with calcium chloride, and fractional distillation. It is a colourless liquid boiling at  $150^\circ-151^\circ$ , and having a not unpleasant odour, resembling that of pure ethyl cyanide (Tollens, *Deut. Chem. Ges. Ber.* v. 621).

*Di-isallyl alcohol*,  $C^6H^{10}O^2$  (Hübner a. Müller, *Ann. Ch. Pharm.* cli. 384).—When dry epichlorhydrin is added drop by drop to sodium immersed in anhydrous ether, the ether distilled off at the end of the reaction, the residuo treated with water to remove the excess of sodium, the whole then evaporated to dryness, the residue digested in absolute alcohol, and the alcoholic solution evaporated, a syrupy liquid is left which distils with partial decomposition at  $218^\circ-225^\circ$ . It has the composition  $C^6H^{10}O^2$ , and appears to be a polymeride formed from two molecules of isallyl-

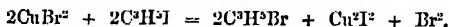
alcohol,  $\begin{array}{c} H^2C \\ | \\ H^2C \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} CHOH \\ | \\ CHOH \end{array}$  (p. 47) arranged in a ring. The action of the sodium on the epichlorhydrin first forms the compound  $C^3H^5NaO^2$ , and on treating this compound



with water, the sodium is replaced by hydrogen, so that the final result may be represented by the equation:



**ALLYL ETHERS.** The *bromide*,  $\text{C}^3\text{H}^5\text{Br}$ , or  $\text{CH}^2=\text{CH}-\text{CH}^2\text{Br}$ , is formed, together with dibromhydrin, by the action of phosphorus bromide on slightly warmed syrupy glycerin (L. Henry, *Zeitschr. f. Chem.* [2] vi. 575). It is also produced from the iodide by the action of cupric bromide in alcoholic solution, a precipitate of cuprous iodide being formed at the same time, and bromine set free:



Part of the liberated bromine, however, unites with the allyl bromide, so that the latter is not obtained pure (Oppenheim, *Deut. Chem. Ges. Ber.* iii. 442).

Allyl bromide heated in a sealed tube at  $100^\circ$  for a few minutes with highly concentrated hydrobromic acid is almost wholly converted into a mixture of two isomeric bodies  $\text{C}^3\text{H}^5\text{Br}^2$ , separable by fractional distillation. One of these is propylene (methyl-ethylene) bromide  $\text{CH}^3-\text{CHBr}-\text{CH}^2\text{Br}$ , which, when treated with excess of potash, yields only allylene; the other, which boils at a higher temperature ( $160^\circ-163^\circ$  at 719 mm., uncorrected), is trimethylene bromide,  $\text{CH}^2\text{Br}-\text{CH}^2-\text{CH}^2\text{Br}$ , which with alcoholic potash forms allyl-ethyl oxide. With barium hydrate this bromide yields trimethylene glycol  $\text{CH}^2\text{OH}-\text{CH}^2-\text{CH}^2\text{OH}$ , a thick, sweet-tasting liquid, boiling between  $208^\circ$  and  $218^\circ$ ; it is the alcohol corresponding to ethylene-lactic and malonic acids (Geromont, *Ann. Ch. Pharm.* clviii. 369).

*Diallyl tetrabromide*,  $\text{C}^6\text{H}^{10}\text{Br}_4$ , heated with solid caustic potash, yields a product containing *dibromodiallyl*,  $\text{C}^4\text{H}^6\text{Br}_2$ . This, when heated with an alcoholic potash solution, is converted into *diallylene*,  $\text{C}^4\text{H}^6$ , an isomeric of benzene. It is a very refractive liquid, boiling at about  $85^\circ$ . It burns with a luminous and smoky flame, and combines explosively with bromine. With an aqueous solution of silver nitrate, it gives a white, amorphous precipitate insoluble in ammonia and exploding when heated below  $100^\circ$  (Henry, *Deut. Chem. Ges. Ber.* v. 449).

*Allyl trichloride*,  $\text{C}^3\text{H}^5\text{Cl}_3$ , is very slowly acted on by chlorine. On dissolving iodine in it, and passing dry chlorine into the heated solution in sunshine, a small quantity of white crystals gradually separates, consisting of perchlorethane,  $\text{C}^2\text{Cl}^6$ . The action of chlorine on trichlorallyl consists therefore in a destruction of the molecule (Oppenheim, *Deut. Chem. Ges. Ber.* iv. 669).

*Allyl cyanide*,  $\text{C}^3\text{H}^5\text{CN} = \text{C}^3\text{H}^3\text{CN}$ .—Rinne a. Tollens (*Zeitschr. f. Chem.* [2] vii. 251) prepare this compound by heating allyl iodide with potassium cyanide to  $110^\circ$  for two days, washing the product, again heating with potassium cyanide, and fractionating after treatment with a few drops of nitric acid. It has a not disagreeable alliaceous odour, boils at  $116^\circ-118^\circ$ , and is converted by aqueous or alcoholic potash into crotonic acid melting at  $71^\circ-72^\circ$ . The allyl cyanide thus prepared is therefore identical with that which Will and Körner obtained by decomposition of myronic acid (1st *Suppl.* 525).

A mixture of allyl chloride with a solution of potassium cyanide in allyl alcohol heated to  $100^\circ$  in a sealed tube, yields a small quantity of the compound  $\text{C}^3\text{H}^5\text{CN} \cdot 3\text{C}^2\text{H}^5\text{O}$  analogous to the ethyl-compound  $\text{C}^2\text{H}^5\text{CN} \cdot \text{C}^2\text{H}^5\text{O}$ , which Gautier obtained (*Bull. Soc. Chim.* [2] ix. 2), together with propionitril, by heating a mixture of potassium ethyl-sulphate and potassium cyanide. This allyl-compound boils at  $95^\circ-96^\circ$ ; it has an extremely pungent odour when first prepared, but after purification by repeated washing with dilute hydrochloric acid and with water, it smells more like mustard. Heated to  $130^\circ$  with hydrochloric acid, it yields a thick oil, together with sal-ammoniac.

A compound of allyl cyanide with *ethyl alcohol*,  $\text{C}^3\text{H}^5\text{CN} \cdot 3\text{C}^2\text{H}^5\text{O}$ , is produced by digesting a mixture of allyl iodide and alcohol with excess of potassium cyanide, and may be separated by fractional distillation. It is a liquid having an agreeable odour like that of allyl cyanide; boils at  $173^\circ-174^\circ$ . It is decomposed by digestion with potash, yielding crotonic acid, ammonia, and alcohol, but no ethylamine (Rinne, *Deut. Chem. Ges. Ber.* vi. 389).

*Allyl-ethyl-oxide*,  $\text{C}^5\text{H}^8\text{OC}^2\text{H}^5$ , agitated in a cooled vessel with cold dilute hypochlorous acid, forms oxethyl-chlorhydrin, or  $(\text{C}^2\text{H}^5)^m\text{Cl}(\text{OH})(\text{OC}^2\text{H}^5)$ , a thick colourless liquid boiling at  $183^\circ-185^\circ$  (Henry, *loc. cit.*).

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*Allyl-methyl oxide*,  $C^3H^5OCH^3$ , obtained by the action of sodium methylate on allyl bromide, is a liquid boiling at  $46^\circ$ . Its dibromide,  $CH^3OC^3H^5Br^2$ , boils at  $185^\circ$ , and yields by distillation over solid caustic soda, *methyl-monobromallyl oxide*, boiling at  $115^\circ$ – $116^\circ$ , together with some *methyl-propargyl oxide*,  $CH^3OC^3H^3$ .

*Allyl-phenyl oxide*,  $C^6H^5OC^3H^5$ , is produced by the action of sodium phenylate upon allyl bromide. It is a colourless, strongly refracting liquid, boiling at  $192^\circ$ – $195^\circ$ , and having the same density as water. It combines with bromine, but products containing brominated phenyl are formed at the same time (Henry).

*Bromallyl and Chlorallyl Alcohols and Ethers* (Henry, *Deut. Chem. Ges. Ber.* v. 186, 449).

*Monobromallyl acetate*,  $C^3H^5Br.C^2H^3O^2$ , is produced by the action of dibromoglycide or epidibromhydrin,  $C^3H^5Br^2$  (which may be regarded as bromallyl bromide,  $C^3H^5Br.Br$ ), upon potassium acetate. It is a mobile liquid, boiling at  $163^\circ$ – $164^\circ$ , and having a pleasant, refreshing odour; it is not acted upon by the chlorides of phosphorus. By distillation with caustic soda it yields *monobromallyl alcohol*,  $CH^3.CBr.CH^2.OH$ , a mobile liquid boiling at  $155^\circ$ , and having also an agreeable odour. By the action of phosphorus pentachloride the alcohol is converted into *monochlorallyl chloride*,  $(C^3H^5Br.Cl)$ , a heavy liquid boiling at  $120^\circ$ , and most probably identical with Reboul's chlorhydrobromoglycide.

By heating the alcohol with an alcoholic potash-solution, a distillate is obtained showing the reactions of the propargyl-compounds, and containing most probably *propargyl-alcohol*,  $C^3H^5OH$ , which, however, could not be isolated.

Dibromoglycide treated with silver nitrate, yields *monobromallyl nitrate*,  $C^3H^5Br.NO^3$ , a liquid having an agreeable odour and sweetish pungent taste:  $C^3H^5Br.Br + AgNO^3 = AgBr + C^3H^5Br.NO^3$ .

By the action of potassium acetate upon dichloroglycide, a mixture of several products is obtained, among them being a small quantity of monochlorallyl acetate; and when dichloroglycide is heated with potassium sulphocyanate, pure monochlorallyl sulphocyanate is produced.

*Monochlorallyl sulphocyanate*,  $(C^3H^5Cl)SCN$ , produced by the action of potassium sulphocyanate on dichloroglycide (chlorallyl chloride), is a colourless liquid boiling at  $185^\circ$ , and having a very pungent smell, like that of mustard-oil. It combines quickly with ammonia, yielding *monochlorothiosinamine*,  $CS \begin{Bmatrix} NH^3 \\ NH.C^3H^5Cl \end{Bmatrix}$ , in colourless crystals, melting at  $90^\circ$ – $91^\circ$ . *Monobromallyl sulphocyanate* boils at  $200^\circ$  and yields a thiosinamine melting at  $110^\circ$ – $111^\circ$ .

*Monobromallyl-ethyl oxide*,  $C^3H^5BrOC^2H^5$ , is obtained by distilling ethyl-dibromhydrin,  $C^3H^5Br^2OC^2H^5$ , with caustic soda. It is a colourless liquid having a pleasant smell, and boiling at  $130^\circ$ – $135^\circ$ . It is easily transformed into propargylether,  $C^3H^5OC^3H^3$ , by heating it with an alcoholic potash-solution.

*Monochlorallyl-ethyl oxide*,  $C^3H^5ClOC^2H^5$ , is formed by the action of alkalis upon ethyl-dichlorhydrin; it boils at  $120^\circ$ .

The formation of these substituted allyl compounds is analogous to that of monochlorpropylene from propylene dichloride. They contain, therefore, the chlorine or bromine combined with the middle carbon atom of the allyl group. This is further proved by the fact, that by the action of sulphuric acid upon pure epidichlorhydrin, monochloracetone is formed, whilst, as Oppenheim has shown, acetone is obtained by acting with sulphuric acid upon monochloro-propylene.

**ALLYLENE.**  $C^3H^4$ .—On the constitution of this hydrocarbon, see Carstanjen, (*J. pr. Chem.* [2] iv. 419; *Chem. Soc. J.* [2] x. 231). Allylene is converted into propionic acid by the action of aqueous chromic acid, in the same manner as acetylene into acetic acid (p. 4). The reaction appears, however, to take place by two stages, the allylene being first converted into allylene oxide,  $C^3H^4O$ , and this, by addition of  $H^2O$ , into propionic acid.

*Allylene oxide*, which is also produced by the action of chromic anhydride on isonally alcohol (prepared by treating allylene with sulphuric acid, &c.), is a mobile neutral liquid, having a pungent odour and boiling at  $62^\circ$ – $63^\circ$ . It is extremely stable, not being acted on by baryta-water at  $150^\circ$ , or when heated in a sealed tube with syrupy potassium hydrate to  $220^\circ$  or even to  $300^\circ$ . It reduces silver nitrate.

*Hydrobromides.*—Allylene unites directly and rapidly in the cold, with a concentrated aqueous solution of hydrobromic acid employed in great excess. With an acid marking  $66^\circ$  Baumé, and at  $0^\circ$ , the process is complete in five or six hours. The oily body obtained is *dihydrobromide of allylene*,  $C^3H^4.H^2Br^2$ , with a small quantity of the monohydrobromide. On rectification, a liquid is obtained, having a density of 1.875 at  $10^\circ$ , and boiling at  $114^\circ$ – $115^\circ$ . This body is isomeric with propylene

bromide,  $C^3H^5Br^2$ , but has a much less fragrant odour, and appears to be identical with Linnemann's methylbromacetol, or *dimethyl-dibromomethane*  $C(CH^3)_2Br^2$ . The dihydrobromide, submitted to the action of alcoholic potash, loses one molecule of hydrobromic acid, and is reduced to *monohydrobromide*,  $C^3H^4.HBr$ , which has a density of 1.39 at  $9^\circ$ , and boils at  $48^\circ$ – $49^\circ$ . Allylene hydrobromide, though isomeric with bromopropylene, is quite a distinct body, having a lower boiling point, and being much more readily acted upon by a concentrated solution of hydrobromic acid (Reboul, *Compt. rend.* lxxiv. 669).

The monohydrobromide is also formed by the action of alcoholic potash on bromopropylene hydriodide,  $C^3H^4Br.HI$ . It unites with hydriodic acid, forming *allylene hydrobromide*,  $C^3H^4.HBr.HI$ , which boils at  $147^\circ$ – $148^\circ$ , and is identical with the hydriodide of bromopropylene. The combination of hydriodic acid with allylene hydrobromide takes place, however, much more energetically than that of the same acid with bromopropylene. Probably the hydriodic acid in the latter case first transforms the bromopropylene into allylene hydrobromide, and then unites with the latter. Allylene dihydrobromide,  $C^3H^4.2HBr$ , is identical with bromopropylene hydrobromide,  $C^3H^4Br.HBr$ , both these bodies, when treated with potash, yielding allylene monohydrobromide (Reboul, *Compt. rend.* lxxiv. 669, 944).

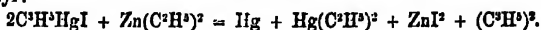
*Hydrochlorides.*—Allylene also unites directly in the cold with concentrated hydrochloric acid, but much less rapidly than with hydrobromic acid. The oily product is a mixture of mono- and di-hydrochloride of allylene, in which the latter largely predominates. On rectification the dihydrochloride is found to boil at  $69^\circ$ – $70^\circ$ , and is probably identical with Friedel's methylchloracetol, or *dimethyl-dichloromethane*,  $C(CH^3)_2Cl^2$  (Reboul).

**ALLYLIN.**  $C^3H^5O^2 = (C^3H^5)^{'''} \left\{ \begin{array}{l} (OH)^2 \\ OC^2H^3 \end{array} \right.$  (Tollens, *Deut. Chem. Ges. Ber.* v. 68),

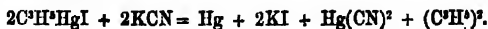
—Obtained from the syrupy liquid which remains after the rectification of crude allyl alcohol, prepared by distilling glycerin with oxalic acid. It is a viscid liquid boiling at  $225^\circ$ – $240^\circ$ , soluble in water, partly decomposed by distillation, with formation of allyl alcohol. Bromine dropped into its aqueous solution unites with it, forming allylin dibromide,  $C^3H^5O^2Br^2$ , which separates as an oil.

Allylin is distinguished from glycerin-ether,  $(C^3H^5)^2O^2$ —likewise a by-product in the preparation of allyl alcohol, and regarded by Linnemann and v. Zotta (*Ann. Ch. Pharm. Suppl.* viii. 252) as identical with it—both by its composition and by its reactions, glycerin-ether not being decomposed by distillation, and not combining with bromine.

**ALLYLMERCURIC COMPOUNDS.** *Mercuric iodallylide*,  $C^3H^5HgI$ , is best obtained by shaking mercury with a mixture of equal volumes of allyl iodide and alcohol. It crystallises from carbon bisulphide and acetone in white scales, which soon turn yellow. It is not acted upon either by phosphorus tribromide or by acetyl chloride or benzoyl chloride. On adding it to a solution of zinc-ethyl in ether, an energetic reaction sets in, the products being mercury, zinc iodide, mercuric ethide, and diallyl:



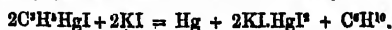
A solution of potassium cyanide acts on mercuric iodallylide quickly in the cold, according to the equation:



Besides these products, two mercury-allyl compounds are probably formed, one of which is liquid, and explodes when the distillation of the diallyl is not stopped in time.

The mercury compounds of allyl attack the skin, but the action becomes perceptible only after 6–8 hours, when painful blisters appear (Oppenheim, *Deut. Chem. Ges. Ber.* iv. 670).

Mercuric iodallylide heated to  $100^\circ$  in a sealed tube with aqueous potassium iodide, yields metallic mercury, potassio-mercuric iodide, and diallyl:



When a mixture of mercuric iodallylide and allyl iodide is heated with iron turnings to  $100^\circ$  for three days, the greater part of the mercuric iodallylide remains unaltered, and only a small quantity of a substance smelling like diallyl is produced. If the same mixture is heated for a day with granulated zinc, a gas is formed which burns with a bright flame. When moist silver oxide is added to mercuric iodallylide under alcohol, and the mixture is shaken, silver iodide is formed, together with an alkaline solution (doubtless containing the base  $C^3H^5HgOH$ ), which, when evaporated over

sulphuric acid, yields crystals soluble in water, together with a large quantity of oil; but the reaction is slow and incomplete. The alkaline solution neutralised with acids yields crystalline salts. The chloride  $C^3H^5HgCl$  is sparingly soluble and is precipitated on adding hydrochloric acid to the alkaline solution (Krasowsky, *Zeitschr. f. Chem.* vi. 527).

**ALLYL-PHENOL.** See PHENOL.

**ALLYL-PHENYL-FORMIC ACID.** See FORMIC ACID.

**ALLYL-SULPHONIC ACID,  $C^3H^5.H.SO^2$ .**—When neutral potassium sulphite, dissolved in a small quantity of water, is boiled with its own weight of allyl iodide till the latter disappears, the liquid, on evaporation on the water-bath, leaves a crystalline residue; and on exhausting with boiling alcohol and cooling, a white salt is obtained, which, after washing with alcohol, has the composition of a mixture of potassium iodide and allyl-sulphite,  $6KI.7K(C^3H^5)SO^2$ . On addition of ether to the alcoholic mother-liquor, a salt of similar appearance is precipitated, which has the composition  $2KI.3K(C^3H^5)SO^2$ . On addition of lead acetate to the aqueous solution of these salts, lead iodide is precipitated; the filtrate decomposed by hydrogen sulphide, evaporated, extracted with alcohol, and precipitated with ether, yields a salt not quite free from iodine; but a pure salt having the composition  $K(C^3H^5)SO^2$  is obtained by decomposing the double iodised compound with warm sulphuric acid, evaporation of most of the excess of acid, extraction with alcohol after neutralisation with potassium carbonate, and precipitation with ether; the product thus obtained is white, indistinctly crystalline, and readily soluble in water.

*Barium allylsulphonate* is a hygroscopic white mass, soluble in water and alcohol, but not in ether; the *lead salt* crystallises from alcohol in golden crystalline plates (A. v. Rad. *Ann. Ch. Pharm.* clxi. 218).

**ALLYL-URETHANES.** See SULPHOCARBONIC ETHERS.

**ALOES.** The two varieties of this drug—namely, Barbadoes aloes, or Liver aloes, *Aloë hepatica*, and Cape or Natal aloes, *Aloë lucida* (1st *Suppl.* 99), contain different crystalline principles, which may be distinguished as barbaloin and nataloin.

**Barbaloin,  $C^{12}H^{10}O^7$ ,** which is the variety discovered by T. and H. Smith, and examined some years ago by Stenhouse (i. 148), may be prepared by dissolving Barbadoes aloes in boiling water slightly acidulated with hydrochloric acid, and evaporating the filtered liquid to a syrupy consistence; in a few days a lemon-yellow mass of barbaloin results, which may be purified by draining, pressure and recrystallisation. By the action of cold fuming nitric acid it is converted into a mixture of aloetic, chrysammic, oxalic and picric acids, the two former of which are but very slightly soluble in cold water. By prolonged boiling with nitric acid, the aloetic acid is finally converted into chrysammic acid, which may, in fact, be more conveniently prepared in this manner from aloin than from crude aloes (Tilden, *Pharm. J. Trans.* [3] ii. 845; *Chem. Soc. J.* [2] x. 488). Barbaloin fused with caustic potash, yields, in addition to orcin and picroxybenzoic acid (1st *Suppl.* 10), a small quantity of alorcinic acid (*infra*).

**Chloraloin,  $C^{12}H^{11}Cl^3O^7$ ,** analogous to the bromaloin discovered by Stenhouse, is obtained by gradually adding aloin dissolved in hydrochloric acid to a mixture of potassium chlorate and fuming hydrochloric acid. After each addition of the aloin, a red coloration is produced, which, however, quickly disappears, the solution assuming a clear orange colour, and depositing in a few minutes a copious crop of yellow granules, the quantity of which increases by standing for a few hours. It may then be filtered off, washed with a little water, and crystallised from warm rectified spirit. The tufts of bright yellow prisms which separate in a few hours are collected and dried by exposure to dry air. They bear, without change of colour or general appearance, a temperature of  $120^\circ$ , and even much higher. They give, by analysis, numbers agreeing nearly with the formula  $C^{12}H^{11}Cl^3O^7.3H^2O$ , the proportion of chlorine being, however, a little too high, probably owing to the presence of a small quantity of a more highly chlorinated compound.

Chloraloin is more soluble in water than bromaloin, and more stable than the original aloin. Thus, although very soluble in aqueous ammonia, it crystallises out but little altered when the ammonia is evaporated, and it may be dissolved in ordinary nitric acid (sp. gr. 1.37) without change of colour. Boiled with nitric acid and silver nitrate, it yields oxalic and picric acids only, without a trace of aloetic or chrysammic acid. In most of the reactions of aloin and of its chloro- and bromo-derivatives, there is a marked resemblance to those of the orcins (Tilden, *Chem. Soc. J.* [3] x. 204).

**Nataloin.**  $C^{24}H^{32}O^{13}$  [ $= 2C^{12}H^{16}O^7 + H^2O$ ].—Natal aloes, moistened with spirit and examined by the microscope, exhibits crystals of a compound which is but slightly soluble in alcohol, so that, on treating the aloes with its own weight of that solvent at  $49^\circ$ , the crystalline principle, nataloin, is readily obtained in a crude state. When purified by crystallisation from hot spirit, it forms thin, bright yellow scales, sparingly soluble in water, benzol, carbon disulphide, chloroform, and ether. It contains no water of crystallisation, melts between  $212^\circ$  and  $222^\circ$ , dissolves in concentrated sulphuric acid, and the addition of a crystal of potassium nitrate to this solution produces a characteristic bright green coloration, rapidly passing through red to blue. Heated with nitric acid it is decomposed, yielding oxalic acid without a trace of picric or chrysammic acid (Flückiger, *Arch. Pharm.* [2] cxlix. 11). According to Tilden, on the contrary (*Chem. Soc. J.* [2] x. 153) it yields picric as well as oxalic acid. The non-production of chrysammic acid shows, however, that this kind of aloin differs essentially from barbaloin.

Another modification of aloin is obtained from crude Zanzibar aloes by slight washing with dilute spirit. When purified by crystallisation from spirit, it forms tufts of needles. It is much more soluble than nataloin, and contains water of crystallisation,  $C^{24}H^{32}O^{13} + 5H^2O$ , which it loses when dried over sulphuric acid, leaving anhydrous Zanzibar aloin,  $C^{24}H^{32}O^{13}$ , isomeric with nataloin. It does not appear to form a substitution-product with bromine; neither does it give with nitric acid the deep red colour exhibited by barbaloin (Flückiger, *loc. cit.*).

**Lign Aloes, Oil of.** See OILS, VOLATILE.

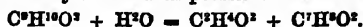
**ALOES-RED.** On the detection of this colour, see COLOURING MATTERS.

**ALORCINIC ACID.**  $C^{21}H^{16}O^8$  (Weselsky, *Deut. Chem. Ges. Ber.* v. 168; *Ann. Ch. Pharm.* clxvii. 65).—This acid, isomeric with melilotic, hydroparacoumaric, phenyl-licetic, xylic, oxymesitylenic, phloretic, and tropic acids, is obtained, in comparatively small quantity, together with orcin and paraoxybenzoic acid, by the action of melting potash upon aloes, and separates in crystalline masses from the mother-liquors of the paraoxybenzoic acid. It dissolves with difficulty in cold water, but readily in boiling water, in alcohol, and in ether, and crystallises from the boiling aqueous solution on cooling, in bulky concentric groups of long needles. It has a sour, somewhat astringent taste. The air-dried acid melts at  $97^\circ$ ; that which has been dried over sulphuric acid melts at  $115^\circ$ . By distillation it yields an oil which soon solidifies to a crystalline mass of the anhydride  $C^{21}H^{16}O^8$ , which melts at  $138^\circ$ , sublimes when heated between two watch-glasses, in light-shining laminae resembling benzoic acid, dissolves slowly in water, and is gradually reconverted into the acid—much more quickly, however, in a solution of alkaline carbonate.

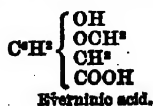
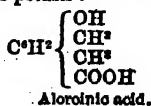
The aqueous solution of alorcinic acid is not coloured by ferric chloride, but, if rendered alkaline, it acquires a characteristic cherry-red colour on exposure to the air. With hypochlorites the aqueous acid produces a splendid purple-red colour, which, however, is destroyed by excess of hypochlorite. A neutralised solution of the acid reduces silver nitrate on gentle heating, and separates cuprous oxide on heating from a solution of potassio-cupric tartrate. The acid in dilute solution is not precipitated by neutral lead acetate, but with the basic acetate it forms a white precipitate which gradually turns red.

Alorcinic acid easily decomposes metallic carbonates. Its barium salt,  $Ba(C^{21}H^{16}O^8)^2 + 6H^2O$ , crystallises in groups of small needles, moderately soluble in water, soluble also in alcohol, insoluble in ether; at  $100^\circ$  it becomes rose-coloured and begins to decompose. The calcium salt,  $Ca(C^{21}H^{16}O^8)^2$ , is more soluble than the barium salt, and crystallises in anhydrous needles. The copper salt,  $Cu(C^{21}H^{16}O^8)^2 + 4H^2O$ , is obtained by decomposing the barium salt with cupric sulphate. The green filtrate, if concentrated and stirred, deposits the salt in emerald-green crystals, but if left at rest it is apt to dry up to a green varnish. The crystals are nearly insoluble in water, but dissolve with moderate facility in ether-alcohol. The alorcinates of the alkali-metals are difficult to purify, on account of the sensibility of the acid to the action of oxygen in presence of strong bases.

Alorcinic acid is resolved by fusion with potash into acetic acid and orcin:



Hence it is nearly related to everninic acid,  $C^{17}H^{10}O^4$ , which likewise yields orcin when fused with potash:



It is probable also that aloreinic acid is one of the first products of the decomposition of aloes by potash, and that the orcin thereby obtained results from the further decomposition of this acid.

*Acetyl-aloreinic acid*,  $C^{11}H^{12}O^4 = C^9H^9(C^2H^3O)O^2$ , is produced by the action of acetyl chloride on aloreinic acid, the action commencing in the cold, and being completed, with strong evolution of hydrochloric acid, on application of heat. After the excess of acetyl chloride has been expelled by heating over the water-bath, there remains a thickish residue, which soon solidifies in the crystalline state, is nearly insoluble in boiling water, but may easily be recrystallised from dilute alcohol.

Acetyl-aloreinic acid crystallises in colourless needles easily soluble in ether. It begins to melt at  $125^\circ$ , but decomposes partially at the same time. By distillation it is resolved into acetic acid and aloreinic anhydride.

**ALUMINITE.** This mineral occurs in many localities near Halle, in white, or more rarely yellowish, crystalline nodules of various shape and size (up to that of the fist), also in strings and plates attached together, between strata and in clefts of the so-called Magdeburg sand. Where this carbonaceous and somewhat pyriteferous sand comes to the surface, and therefore in contact with the air, there is formed, by the mutual action of the atmospheric gases, the finely divided iron pyrites, and the fine particles of lignite and clay (kaolin particles and mica), a hydrated basic aluminium sulphate, namely aluminite. In these sands, which may be called 'aluminite sands,' the aluminite occurs so abundantly, where the conditions are favourable to its formation, that its nodules almost displace the sand (Laspeyres, *Jahrbuch f. Mineralogie*, 1872, 951.)

**ALUMINIUM.** The reactions of this metal with certain metallic solutions have been examined by A. Cossa (*Il nuovo Cimento* [2] iii. 75, 228; *Zeitschr. f. Chem.* [2] vi. 380, 443).

*Copper salts.*—A solution of cupric nitrate or sulphate is not acted on by aluminium at first, but in about two days, slowly growing crystals are deposited on the plate, consisting partly of dendrites, but mostly of well-defined octohedrons. From the solution of the nitrate there separates, besides metallic copper, a basic salt in the form of a green insoluble powder. From cupric chloride the copper is immediately precipitated, and likewise from the acetate, though the deposition goes on more slowly. The reduction also takes place immediately when a small quantity of a very dilute solution of an alkaline chloride is added to the sulphate or nitrate, and if a sufficient quantity of aluminium is present the precipitation is complete.

*Lead salts.*—From solutions of the nitrate or acetate aluminium slowly precipitates the lead in crystals, and immediately from a solution of the chloride. An alkaline solution of lead chromate is immediately decomposed by aluminium, with formation of metallic lead and chromic oxide.

*Mercury salts.*—From solutions of mercuric chloride, cyanide or nitrate, aluminium first throws down metallic mercury, which then unites with the aluminium, forming an amalgam, which decomposes water at ordinary temperatures, and oxidises in the air with great rise of temperature.

From an alcoholic solution of mercuric chloride the precipitation of the mercury is much quicker than from an aqueous solution, and is attended with considerable rise of temperature. Mercury is also thrown down by aluminium from a solution of mercuric iodide in potassium iodide. Aluminium foil acts very strongly on vapour of mercuric chloride, mercury being set free and aluminium deposited on the colder parts of the tube: the reaction is attended with so much heat that the excess of aluminium melts into globules.

*Silver salts.*—From slightly acid or from neutral solutions of silver nitrate, aluminium throws down the silver in the form of dendrites. Whether the solution be concentrated or dilute, the precipitation of the silver does not begin till about six hours after the immersion of the aluminium. From an ammoniacal solution of silver chloride the silver is immediately precipitated as a crystalline powder; aluminium also throws down the silver from an ammoniacal solution of silver chromate.

When aluminium is brought in contact with fused silver chloride, great heat is evolved, and silver is separated in melted globules.

*Thallium salts.*—A plate of aluminium immersed in a slightly acid solution of thallium sulphate, becomes coated in ten days with regular octohedrons of thallium alum. From a solution of thallium chloride at  $90^\circ$ , metallic thallium is precipitated.

*Zinc salts.*—From an alkaline zinc-solution, aluminium easily separates the metal.

*Aluminium Amalgam* may be formed either by bringing aluminium in contact with mercury containing a small quantity of sodium (iii. 886), or by Joule's method of

electrolysing the solution of an aluminium salt, with mercury for the negative pole (*Chem. Gaz.* 1850, 339); but the best method is to heat the two metals together in a gas which does not act on either of them. A piece of aluminium foil is placed at the bottom of a thick-walled test-tube, and well-dried mercury is poured upon it, the tube having been previously drawn out in the middle to prevent the aluminium from rising to the surface of the mercury. The air is then expelled from the tube by a stream of dry carbonic anhydride, and the tube is heated without interrupting the current of gas, till the aluminium is completely dissolved.

Aluminium-amalgam decomposes in contact with air or with water more quickly than sodium-amalgam. When a few drops of an amalgam containing but a small proportion of aluminium are left in contact with moist air, gelatinous opalescent excrescences of pure aluminium hydrate are seen to form on their surface, exhibiting, both in their form and mode of growth, considerable resemblance to the so-called Pharaoh's serpents. The aluminium hydrate thus obtained is perfectly soluble in alkalis and acids. When, on the other hand, the amalgam containing a small proportion of aluminium is brought in contact with a large quantity of water, transparent iridescent laminæ, also having a crystalline aspect and consisting of the hydrate  $Al^3H^4O^7$ , form in the course of two days. These laminæ give up all their water when heated, retaining their crystalline aspect, but becoming much less easily soluble in alkalis and acids (Cossa, *loc. cit.*).

On compounds of Aluminium with Zirconium, see ZIRCONIUM.

An impure chloride of aluminium, containing calcium and sodium salts, and known commercially as 'chlor-alum,' is now much used as a disinfectant.

**ALUMS.** See SULPHATES.

**AMARIC ACID.**  $C^{12}H^{12}O^7$ , or  $C^{12}H^{10}O^4, H^2O$ .—An acid formed, together with deoxybenzoin, when benzamarone is heated for a long time with alcoholic potash, unaltered benzamarone being first deposited; then, on addition of water, deoxybenzoin; and finally after evaporation, potassium amarate, in the form of an oil which solidifies on cooling in white scales insoluble in the excess of potash. From the solution of this salt amaric acid is thrown down by all acids, even acetic, in the form of a white, curdy, crystalline precipitate,  $C^{12}H^{12}O^7$ , insoluble in cold water, but soluble in boiling alcohol, ether and acetic acid. It loses 1 mol. water at  $125^\circ$ , and melts at  $140^\circ$ , losing a further  $1\frac{1}{2}$  mol. of water, and then solidifies in the crystalline form. After being once heated to  $140^\circ$  it melts at  $155^\circ$ , is no longer soluble in 15 parts of 90 per cent. alcohol, dissolves in ammonia at  $110^\circ$ – $120^\circ$ , also in potash-solution, forming potassium amarate. Potassium amarate,  $C^{12}H^{12}K^2O^6 + 2H^2O$ , separates from boiling ether, either in luncelle, or as an oil gradually solidifying in warty groups. The barium, lead, and silver salts are curdy, loose, amorphous precipitates, which gradually become heavy and crystalline. The silver salt,  $C^{12}H^{12}Ag^2O^6$ , is white and almost insoluble in water and alcohol. The barium salt crystallises well from alcohol. All the salts are bitter (Zinin, *Zeitschr. f. Chem.* [2] vii. 538).

**AMBYGONITE.** See PHOSPHATES OF ALUMINIUM.

**AMBYLSTEGITE.** A rhombic mineral from a spheroidal mass, found near Lake Taach. It has the axial ratio  $0.971 : 1 : 0.570$ , and exhibits the faces,  $P, 2P_2, \bar{P}_2, \bar{P}_3, \infty P, \infty \bar{P}_2, \frac{1}{2}P_\infty, \infty P_\infty, \infty \bar{P}_\infty$ . Cleavage not determined; fracture conchoidal; lustre adamantine vitreous; colour brown to reddish brown streak grey, inclining to green; hardness nearly equal to that of quartz; not decomposable by hydrochloric acid; difficult to fuse before the blowpipe. The powder, freed by the magnet from intimately admixed magnetic iron ore, has a sp. gr. of  $3.454$  at  $20^\circ$ . The mineral is also accompanied by oligoclase and mica, less frequently with iron-glance and augite. Its analysis leads to the formula  $16RSiO^3 \cdot Al^2O^3$  [where  $R = 1Mg + 1Fe$ ], which is that of an aluminous augite:

	$SiO^2$	$Al^2O^3$	$MgO$	$CaO$	$FeO$
Found	49.8	5.05	17.7	0.15	25.6 = 98.30
Calculated	48.99	5.25	16.35	—	29.41 = 100

(G. vom Rath, *Pogg. Ann.* cxxxviii. 529). V. von Lang, on the other hand (*ibid.* cxxxix. 319), regards the mineral as identical with hypersthene.

**AMEROSITE.** A resin from Charleston, South Carolina. It is yellowish-brown externally, clove-brown internally; semi-transparent. Melts at  $238^\circ$ , giving off succinic acid and a yellow oil. Burns with a yellowish-white light, with a fragrant odour, and without leaving any ash (C. U. Shepard, *Sul. Am. J.* [2] i. 273).

**AMETHENIC ACID.**  $C^8H^{10}O^2$ .—An oily acid, isomeric with ananthylic acid, obtained, together with carbonic and acetic acids and a neutral oil, by the

oxidising action of a mixture of potassium dichromate and dilute sulphuric acid on diamylene. It may be separated from the neutral oil by solution in caustic soda, and precipitation with a mineral acid. It is partially decomposed by distillation, and therefore does not exhibit a constant boiling point, but volatilises with steam without decomposition.

Amethenic acid differs from cenanthylic acid by exhibiting only very feeble acid properties, its salts being decomposed even by carbonic acid. The potassium, ammonium, calcium, and magnesium salts are crystalline and readily soluble in water; the sodium, barium, strontium, and copper salts are amorphous gum-like masses; also very soluble; the mercury, cadmium, zinc, lead and silver salts are white amorphous precipitates.

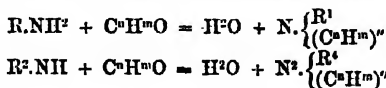
By subjecting this acid to the further action of chromic acid solution, it is completely oxidised to carbonic and acetic acids, together with a small quantity of a crystalline acid different from succinic acid. When amethenic acid is boiled for several days with concentrated nitric acid, nitrous fumes are evolved, and it is converted into a reddish-yellow oil, which appears to be a nitro-product. On heating amethenic acid with phosphorus pentachloride, hydrochloric acid is evolved, and a colourless, very unstable, oily chloride is formed, which soon turns brown, and evolves hydrochloric acid (W. v. Schneider, *Ann. Ch. Pharm.* clvii. 185).

**AMIDODICYANIC ACID.** See CYANIC ACID.

**AMINES.** *Diagnosis of Primary, Secondary, and Tertiary Amines* (Hofmann, *Deut. Chem. Ges. Ber.* iii. 762).—Primary amines are alone capable of yielding isocyanides when treated with chloroform and potash-ley (1st Suppl. 528). This reaction being extremely delicate, and the odour of the isocyanides being quite unmistakable, though it varies to some extent with different radicles, the presence of a primary amine may be easily distinguished. It is only necessary to dissolve a few centigrams of the base in alcohol, and mix the solution with alcoholic potash or soda in a test-tube, and having added a few drops of chloroform, to warm gently. If a primary amine is present, a violent reaction occurs, and vapours of isocyanide, recognisable by their simultaneous effect upon the nose and the tongue, are at once evolved. If in this experiment the characteristic odour of an isocyanide is not perceived, the question remains whether the base under examination is a secondary or tertiary amine. In this case advantage may be taken of the formation of isosulphocyanates. Both *primary* and *secondary* amines, when treated with alcoholic carbon bisulphide, yield isosulphocyanates analogous to mustard-oil, the peculiar odour of which is easily recognisable. The experiment is made by dissolving a few centigrams of the base in alcohol, mixing the solution with about an equal volume of carbon bisulphide, and evaporating a part of the alcohol. The residual liquid is then heated with an alcoholic solution of mercuric chloride. If a primary or secondary amino is present, the irritating odour of the isosulphocyanate is at once perceived. This reaction, however, is not quite general. The first reaction described above is common to all primary amines, whether belonging to the fatty or to the aromatic series; but in the case of the secondary bases, the formation of sulphocyanates takes place only with amines of the fatty series, or with mixed amines. To distinguish between secondary and tertiary aromatic amines, which do not yield sulphocyanate, recourse must be had to the method of treatment with alcoholic iodides; this, however, is very troublesome, inasmuch as considerable quantities of substance must be used, mixed products are frequently obtained, and a weight-analysis must be made after purification; a further disadvantage is, that the whole operation must be repeated for each hydrogen-atom.

The following mode of discrimination, depending on the reaction of amines with aldehydes, is given by Schiff (*Ann. Ch. Pharm.* clix. 158):—

The reaction of aldehydes on primary and secondary amines may be expressed by the following general equations, in which R denotes a monatomic alcohol-radicle:—



These reactions in many instances occur at the ordinary temperature, or at temperatures but little elevated, so perfectly that the water actually separated differs from the theoretical amount by only an inappreciable quantity. The aldehyde most convenient for quantitative estimation based on this principle, an account of its easy purification, high molecular weight, slight volatility, and comparative unalterability, is *cenanthic aldehyde*. A recent estimation of its specific gravity gives the number 0.8257 at 13°, whence its molecular volume is calculated as 139.

139 vols. of cenanthic aldehyde represent, according to the above equations, two



atoms of hydrogen in the form of water, or 0.7 c.c. represents 0.01 gram of hydrogen: hence if the molecular weight of a base (or a multiple thereof) in centigrams be weighed out, every 0.7 c.c. of *œnanthol* employed for perfect action will represent *one* atom of typical hydrogen; or if 69.5 c.c. of *œnanthol* are dissolved in benzene to 100 c.c. then each c.c. of the mixture used will represent *one* centigram of typical hydrogen.

The mode of analysis is as follows: 2 to 4 grams of the base are weighed in a small test-tube, and dissolved in 2 to 3 times their bulk of benzene; a few grams of fused calcium chloride in lumps the size of peas are added, and lastly the *œnanthol* solution is dropped in from a burette divided into  $\frac{1}{50}$  c.c.; each drop produces a thick turbidity from separation of water, which is readily taken up by the calcium chloride on gentle agitation; as soon as no more turbidity is produced, the titration is finished.

By this means satisfactory results have been obtained in the titration of aniline, diaminiline, aniline, toluidine, ethylamine, naphthylamine, and toluylendiamine. For example, with *aniline* boiling constantly at 185° to 186°, but containing a small quantity of toluidine,

2.312 grams required	3.4 c.c. <i>œnanthol</i> :	calculated	3.45 c.c.
2.240 "	3.25 "	"	3.34 "

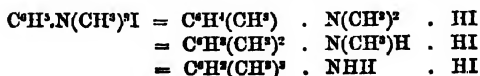
Hence 1 molecule = 93 grams represents 1.95 grams of typical hydrogen, instead of 2 as required by theory.

The same reaction may be employed in the approximate analysis of mixtures of bases; by this means it is shown that distillation alone will not suffice for the separation of diethylaniline and ethylaniline, several per cent. of the latter base being retained; this may, however, be separated by addition of *œnanthol*, as the heptene-diethyl-diphenylamine produced does not volatilise at the boiling point of diethylaniline; similarly ethyl-aniline, though of constant boiling point, always retains a little diethylaniline.

It is necessary that fused calcium chloride be used, the ordinary spongy substance absorbing some of the base, and preventing the complete action of the *œnanthol*; it is best not to add the calcium chloride at first, but to begin by adding a little *œnanthol*, which sets free some water; the calcium chloride is then dropped in, and becomes covered with an aqueous layer, after which the operation proceeds readily; if the calcium chloride be directly added to the dry benzene solution, its surface becomes moistened by the benzene, and the absorption of water proceeds much less quickly. A certain amount of turbidity is always produced on adding *œnanthol* to benzene, even though the latter already contains *œnanthol*; this appearance is in practice distinguishable from the turbidity caused by the evolution of water.

The behaviour of triamines with *œnanthol* has been studied only in the case of rosaniline (see 1st Suppl. p. 908).

*Synthesis of Aromatic Monamines by Intramolecular Atomic Interchange* (A. W. Hofmann, *Proc. Roy. Soc.* xxi. 47; *Deut. Chem. Ges. Ber.* v. 704).—When trimethylphenyl-ammonium iodide,  $C^6H^3.N(CH^3)^3I$  (prepared from pure dimethylaniline and methyl iodide), is heated in a sealed tube to 200°, no change takes place, but if it be heated for a day to 200°–230° or higher, changes ensue represented by the following equations:—



that is to say, there is formed: first, the hydriodide of the tertiary base, dimethylated methylaniline or dimethyl-toluidine; then the hydriodide of the secondary base, monomethylated dimethylaniline or methyl-xylidine; and, finally, the hydriodide of the primary base, trimethyl-aniline or cumidine. The essential character of the reaction is therefore an intramolecular change in the position of the methyl groups. According to the duration of the process there are incorporated in the benzene-nucleus: first, the methyl group of the alcoholic iodide, and then successively the two methyl groups situated in the ammonia residue or lateral chain. Thus the action of heat on the quaternary ammonium compound affords the means of rising from the benzene series to the toluene, xylene, and cumene series, or generally (for the reaction may probably be utilised in many other cases) of passing from a less carbonated to a more carbonated series of compounds.

1. The products formed at 220°–230° yielded when decomposed by alkalis an oily mixture of bases boiling between 200° and 230°. The lowest boiling fraction finally obtained boiled at 186°, gave a platinochloride agreeing in composition with that of dimethyl-toluidine, and when treated with methyl iodide produced a quaternary iodide

having the composition  $C^6H^4(CH^3)_2.N(CH^3)_2I$ , which is that of the iodide of trimethyl-tolylammonium.

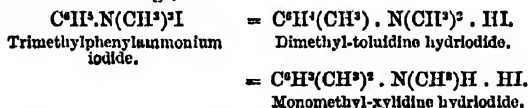
2. The higher-boiling portions were not completely separable by fractional distillation. Portions collected at the temperatures  $200^\circ-203^\circ$ ,  $203^\circ-208^\circ$ ,  $208^\circ-212^\circ$ ,  $212^\circ-220^\circ$ , were treated with methyl iodide, whereby crystalline solid products were obtained, which all had the composition of trimethyltolylammonium iodide, and yielded the corresponding platinum salt. These iodides were mixed together, decomposed by silver hydrate, and the resulting hydrates decomposed by distillation. A tertiary base was thus produced, boiling constantly at  $205^\circ$ , and having the same composition as the dimethyl-toluidine boiling at  $186^\circ$ . Hence two isomeric dimethylised toluidines are formed by the action of heat on trimethylphenylammonium iodide.

To decide whether either of these corresponds with the dimethylised toluidine obtained by methylising solid toluidine, some of this latter was prepared from pure solid toluidine by the action of methyl iodide, and was found to boil at  $207^\circ-208^\circ$ . This was converted into trimethyltolylammonium iodide, which was decomposed by silver hydrate and distillation, furnishing a pure dimethyl-toluidine boiling constantly at  $210^\circ$ . This base resembled in smell the former one boiling at  $205^\circ$ , but differed from the one boiling at  $186^\circ$ . It is thus not improbable that three dimethyl-toluidines have been obtained; but until the dimethylised bases corresponding with the other two toluidines have been investigated, it cannot be said with certainty that the bases boiling at  $205^\circ$  and  $210^\circ$  are really isomeric. All three dimethylised toluidines remained liquid when cooled to  $-10^\circ$ .

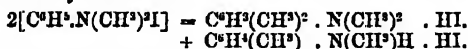
The above-mentioned fractions between  $203^\circ$  and  $220^\circ$  yielded, on treatment with methyl iodide in excess, not only the crystalline trimethyltolylammonium iodide, but also a small quantity of a base which only combined with methyl iodide with great difficulty. This base boiled at  $196^\circ$ , and gave numbers agreeing with the formula of

dimethyl-xylidine,  $\left. \begin{array}{c} C^6H^3(CH^3)_2 \\ CH^3 \\ CH^3 \end{array} \right\} N$ . At  $100^\circ$  it did not combine at all with methyl iodide, but at  $150^\circ$  a small portion became converted into a quaternary iodide, which furnished the platinum salt of trimethyl-xylylammonium.

The formation of dimethylated toluidines and monomethyl-xylidines is due to intramolecular atomic interchange, thus:



The formation of dimethyl-xylidine is due to a secondary reaction, two molecules of trimethylphenylammonium iodide splitting up into the hydriodides of dimethyl-xylidine and monomethyl toluidine:

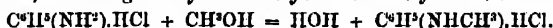


For comparison, dimethyl-xylidine was prepared by the action of methyl iodide on xyldine from commercial aniline oil. This xyldine, boiled at  $216^\circ$ , and the dimethyl-xyldine obtained from it at  $203^\circ$ , or  $7^\circ$  higher than that from trimethylphenylammonium iodide; it readily united with methyl iodide to form a quaternary iodide.

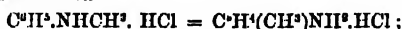
3. When the isomeric transformation of trimethylphenylammonium iodide was effected at a temperature of about  $335^\circ$  (melting point of lead), a further action was noticed, and also the production of several bye-products by secondary reactions. On distilling with water the acid product of the action, a considerable quantity of hydrocarbons, partly solid, partly fluid, was obtained. When the residue was distilled with caustic soda, a mixture of bases distilled, the principal portion of which boiled at  $217^\circ-230^\circ$ , and furnished a crystalline hydrochloride, from which was isolated a base boiling constantly at  $225^\circ-227^\circ$ . This was a cumidine,  $\left. \begin{array}{c} C^6H^2(CH^3)_2 \\ H_2 \end{array} \right\} N$ , which was shown to be a primary base by methylation. The dimethyl-cumidine thereby produced boiled at  $213^\circ-214^\circ$ , and absolutely refused to combine with methyl iodide to form a trimethylcumylammonium iodide. The dimethyl-cumidine and dimethyl-xyldine obtained in the manufacture of dimethyl-aniline, on the other hand, readily unite with methyl iodide, forming quaternary compounds. The cumidine thus obtained from aniline did not yield a trace of colour by the action of corrosive sublimate; but when a mixture of this cumidine and pure aniline was similarly treated, a beautiful carmine-red colouring matter resulted.

Another example of the atomic interchange above described is afforded by the con-

version of aniline into toluidine. When pure aniline hydrochloride is heated to 230°-250° for several hours with methyl alcohol, a yellow transparent honey-like mass is formed, consisting chiefly of methylaniline hydrochloride:



On heating the contents of the tube to 350° for a day, a crystalline hydrochloride is formed by the transformation



in short, *methylaniline becomes converted into toluidine*.

After recrystallisation from water, this toluidine melts at 45°; when, however, the hydriodide of methylaniline is similarly treated, solid toluidine is not formed, but one of the liquid modifications.

The bye-products of the action of heat (about 330°) on trimethyl-phenylammonium contain, amongst other substances, a crystalline primary amine of constitution  $\text{C}^6(\text{CH}^3)^3.\text{NH}^2$ , and a beautifully crystallised hydrocarbon melting at 136° and boiling at 230°-240°, which gives numbers agreeing with the formula  $\text{C}^6(\text{CH}^3)^6 = \text{hexmethyl-benzene}$  (Hofmann, *Proc. Roy. Soc. xxi. 54*; *Deut. Chem. Ges. Ber. v. 720*).

**AMMELINE**,  $\text{C}^6\text{H}^5\text{N}^3\text{O}$ . See CYANURAMIC ACIDS (ii. 287).—*Triethyl-ammeline*,  $\text{C}^6\text{H}^5(\text{C}^2\text{H}^5)^3\text{N}^3\text{O}$ , is formed by the action of hydrochloric acid on triethyl-melamine either by prolonged contact in the cold, or by boiling for a short time:



(See 1st Suppl. 808, where ammeline is erroneously printed *ammelide*.)

**AMMONIA**. *Detection*.—A very delicate test for ammonia is afforded by an aqueous solution of *phenol*. On adding to a liquid containing the smallest quantity of ammonia, or an ammoniacal salt, a few drops of this solution and then a small quantity of a filtered solution of chloride of lime, the liquid becomes green, especially when warmed (Böttger, *N. Repert. Pharm. xxi. 50*).

Guyot (*Zeitschr. anal. Chem. ix. 253*) recommends, as a test for ammonia, an acid solution of *mercuric nitrate* to which potassium bromide is added till the precipitate formed at first is redissolved, and then caustic potash till a permanent orange-yellow precipitate begins to form. With this solution the smallest traces of ammonia produce a white precipitate which remains floating in the liquid for a while, but soon settles to the bottom. Lime and baryta produce in the same liquid only a faint yellowish white turbidity.

Paper stained with alkanina-red is also a very delicate test for ammonia (p. 43).

*Estimation*.—W. Knop (*Zeitschr. anal. Chem. ix. 225*) employs for the estimation of ammonia, especially when several determinations are required to be made in a short time, a solution of *barium* or *sodium hypobromite*. The form of apparatus used in the estimation varies accordingly as the nitrogen-compound under examination is volatile or not. For volatile compounds, the reaction-vessel, A, consists of a wide-necked glass flask, which has a capacity of 250 cub. cent., and can be closed by a perforated caoutchouc stopper. Through this stopper passes a glass tube 12 cent. long and 1.5 cent. in diameter, drawn out to a point at the top, and provided with a stop-cock below the point. Into this flask another vessel, B, can be passed with its mouth downwards by means of a looped string. The mouth of this second vessel is cut off in a slanting direction, and is closed by a circular or oval glass plate fitted closely to it by means of tallow-grease.

To perform the analysis, 20 or 40 cub. cent. of the liquid under examination are introduced into the vessel B, which is then filled up to the mouth with water in case it is not already quite filled by the solution; and the glass plate, previously greased, is pressed upon the oblique edge, so as to rest upon it eccentrically. The vessel B is then introduced, with its mouth downwards, into A, into which 50 cub. cent. of the brominated liquid, and a sufficient quantity of water, have previously been poured. The quantity of liquid in the vessel A must be such that the spaces between its surface and the caoutchouc stopper shall not exceed 15 cub. cent. The stop-cock is then opened and the vessel A is immersed in a cylinder of water, the water reaching above the stop-cock, and the whole is left at rest for a few minutes, so that the air in the glass tube may take the temperature of the water. This tube is then connected with a graduated glass tube standing over mercury (the azometer); the glass plate which closes the inner vessel is made to drop off by shaking the apparatus; and after the first violent evolution of gas has slackened, the vessel A, with closed stop-cock, is inverted, so that all the gas may escape out of B. Connection having again been made with the azometer, the vessel A, after agitation for a while, is once more immersed in the water, and the quantity of gas collected in the azometer is read

off. Correction for temperature is indispensable; that for variation of barometric pressure is in many cases quite unnecessary. By working with three such apparatus at once, two ammonia determinations may easily be made in a quarter of an hour. The same method may be used for the determination of the nitrogen in urea.

For the estimation of ammonia and non-volatile nitrogen compounds, glass vessels are used, divided by a vertical partition into two cells, one containing the compound to be examined, the other the brominated solution.

The solution of barium hypobromite for this process is prepared by introducing 600 grams of barium hydrate into 2 litres of water, adding 100 cub. cent. of bromine, agitating, and then immediately pouring in a previously prepared and cooled solution of 300 grams of barium hydrate in a litre of hot water. The bromine disappears immediately, and a golden-yellow solution is formed. In making an experiment, it is advisable to add to the cell containing the brominated solution a few grams of barium hydrate.

The solution of sodium hypobromite is prepared by mixing a previously cooled solution of 100 grams of sodium hydrate in 250 cub. cent. of water with 25 cub. cent. of bromine. Of this solution, 50 cub. cent. diluted with 200 cub. cent. water are sufficient to liberate 130 to 150 cub. cent. gas from a solution of sal-ammoniac. If the quantity of gas evolved in the analysis does not exceed 15 to 20 cub. cent., this quantity of solution will therefore suffice for six or seven determinations in succession. The error arising from absorption of the nitrogen gas is very small.

*Solution of Metals in Liquid Ammonia.*—According to Seeley (*Chem. News*, xxiii, 160) the alkali-metals dissolve in anhydrous liquid ammonia, without definite chemical action, just as salt dissolves in water, and are left behind with their original appearance and character when the liquid is evaporated. An iron retort, filled with anhydrous chloride of calcium saturated with ammonia at 0°, had a stout glass tube connected with its turned-down neck by means of a screw coupling. This glass tube served to contain the metal or other substance to be acted on by the ammonia. When sodium was subjected to the condensing ammonia, it increased in bulk, became dark-coloured and pasty, and finally formed a homogeneous mobile liquid, of a lively blue colour, both by reflected and transmitted light. On reversing the process by cooling the ammonia-generator, the ammonia gradually evaporates out of the liquid, and the changes observed during the condensation reappear in the reverse order, till at last the sodium is restored to its original bright metallic state. If the evaporation be conducted slowly, the metal is left in crystals. Potassium and lithium behave like sodium. The blue solution of sodium acts as a very powerful reducing agent on metallic salts. The blue liquids obtained in like manner by Weyl (v. 329) and regarded by him as definite alloys of ammonium, were, in all probability, solutions of the several metals in liquid ammonia.

*Action of various Metallic Salts on Ammonia-salts.*—The action of sal-ammoniac at high temperatures on various metallic oxides and salts was examined by H. Rose (*Pogg. Ann.* lxxiii, 582), who found that, for the most part, chlorides of the respective metals were formed, some of which, e.g. the chlorides of ammonium, iron, &c., were readily volatilised; also that basic oxides of the formula  $M^xO$ , such as  $CoO$ ,  $NiO$ ,  $MnO$ ,  $FeO$ , and oxides of the formulae  $(M^x)^xO$ , such as  $Cu^2O$ , decompose ammonium chloride, when heated in an aqueous solution, with evolution of ammonia gas and formation of fixed metallic chlorides, whereas not one of the sesquioxides has this power.

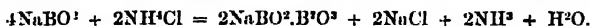
Rose also found that borax is not changed when ignited with ammonium chloride; that sodium phosphate is converted into sodium chloride and a little phosphorus chloride, whilst calcium phosphate is not affected; and that alkaline chromates leave chromic oxide and alkaline chlorides.

Bolley observed (*Ann. Ch. Pharm.* lxxviii, 122) that free ammonia is evolved on mixing solutions of borax and ammonium chloride in the proportions of 1 mol. of the former to one of the latter; the solution, when slowly evaporated, deposited crystals requiring five or six parts of water for their solution, and exhibiting the composition  $Na^2O \cdot 4B^2O^3 + 10aq.$  or  $2NaBO_2 \cdot 3B^2O^3 + 10aq.$  The solution of this salt had no action, either upon litmus or upon turmeric paper, and on the addition of *dilute* sulphuric or nitric acid, gave a white precipitate of boric acid. Bolley also found that an excess of sal-ammoniac converts borax entirely into sodium chloride and boric acid.

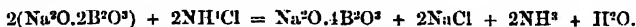
Woodcock (*Chem. Soc. J.* [2] ix, 786) finds that various other salts containing fixed bases, when brought together, in the dry state, or in aqueous solution, with ammonium chloride, likewise decompose the latter, with formation of fixed metallic chlorides and evolution of gaseous ammonia.

When 4 mol. sodium metaborate (prepared by igniting borax with sodium nitrate, till the whole of the latter was decomposed) and 2 mol. sal-ammoniac were heated

together in a retort, ammonia was abundantly evolved, and the whole decomposed rapidly and completely, leaving a residuo of baborate and chloride of sodium: thus—



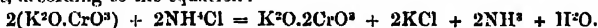
When 2 mol. borax and 2 mol. sal-ammoniac are heated together, Bolley's tetraborate is produced:



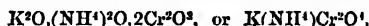
Normal and acid borates may be advantageously employed, instead of lime, for liberating ammonia from its salts, the reaction being complete, and not attended with frothing.

*Trisodic and hydrosodic phosphate* readily decompose ammonium salts, but in the case of the latter, the decomposition is not complete. 3.345 grams of common sodium phosphate distilled from an aqueous solution with .5 gram of ammonium chloride, yielded ammonia corresponding only to 75.69 per cent. of the ammonium chloride employed. This experiment, viewed in connection with the known fact that a solution of microcosmic salt is capable of yielding ammonia when boiled in aqueous solutions, probably giving rise to the formation of dihydro-sodic phosphate, appears to show that the tendency to form acid salts, which is so pronounced in the borates, as to yield (according to Bolley) boric acid by the continuous action of sal-ammoniac upon a solution of borax, does not hold good in the case of phosphates.

The *normal chromates of the alkali-metals*, as well as other soluble and insoluble metallic chromates, evolve ammonia when distilled in aqueous solution with ammonium salts, metallic chlorides being formed, and an acid chromate or bichromate being left, according to the equation:

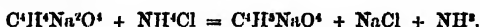


The quantity of ammonia evolved is, however, always less than the theoretical quantity, probably in consequence of the formation of ammonio-potassic chromate,



The action upon ammonium chloride just described is not confined to normal alkaline chromates, inasmuch as insoluble chromates, such as barium or lead chromate, likewise eliminate ammonia when boiled with sal-ammoniac, with formation of acid chromates; ignited lead chromate appears to eliminate ammonia more quickly than the precipitated chromate.

Ammonia is also given off when normal sodium succinate is heated with sal-ammoniac in aqueous solution: thus—



Normal potassium tartrate and citrate act in the same manner.

*On the action of Ammonia on Phosphorus*, see PHOSPHORUS.

*Quantities of Ammonia evolved from various Animal Fluids under the influence of Potash and of Potassium Permanganate* (Wanklyn, *Chem. Soc. J.* [2] x. 646).—When an animal fluid is mixed with excess of potash, and the mixture, after being evaporated down, is kept for some time at a temperature of 160°, a certain quantity of ammonia is evolved, and a further quantity may be obtained by boiling the residue with an alkaline solution of potassium permanganate. For certain animal fluids the quantity of ammonia yielded by a given weight or volume is characteristic; so likewise are the relative quantities of ammonia evolved by the action of caustic potash and of the permanganate. These reactions afford two criteria which may be of some importance in practical biology, especially in enquiries connected with medical jurisprudence.

Of all the animal fluids, urine is the only one that yields a large proportion of ammonia to caustic potash. On the other hand, this liquid is distinguished by the smallness of its yield of ammonia to potassium permanganate.

Milk yields about half as much ammonia to potash as to permanganate.

Blood yields about one-fifth as much ammonia to potash as to permanganate.

White of egg, moist, just as it occurs naturally, gives about one-fourth as much ammonia to potash as to the permanganate.

Gelatin gives no ammonia (or only the least trace) to potash, but a good quantity to permanganate.

It is remarkable, also, that if the preliminary heating to 160° with caustic potash be omitted, and the boiling with permanganate be at once proceeded with, only that

quantity of ammonia is obtained which would have been yielded to permanganate if the entire process had been gone through.

The experiments, which may be performed on very small quantities of liquid, are conducted as follows:—5 cub. cent. of the animal fluid are mixed with water in a 500 cub. cent. flask, and diluted up to the 500 cub. cent. mark, thereby forming a dilute solution, whereof 1 cub. cent. contains  $\frac{1}{100}$  cub. cent. of the animal fluid; 5 or 10 cub. cent. of this dilute liquid are usually taken for one experiment, and a small retort fitted to a small Liebig's condenser is used. The retort is heated in an oil-bath, and the ammonia measured by Nessler's test.

The quantities of ammonia evolved from various liquids thus treated are given in the following table:—

Name of fluid	Ammonia by potash at 150° C.	Ammonia by permanganate of potassium
Urine (human) . . . . .	0.90 gram.	0.05 gram.
Milk of cow. . . . .	0.13 "	0.28 "
Blood of sheep . . . . .	0.46 "	2.20 "
Liquid white of egg (hen) . . . .	0.32 "	1.30 "
Dry solid gelatin (100 grams) . .	0. "	10. "

On the compounds of Ammonia with Ammonium Nitrate, see NITRATES.

On the composition of Ammonium Amalgam, see R. Routledge (*Chem. News*, xxvi. 210; *Chem. Soc. J.* [2] xi. 135).

**AMYL ALCOHOLS.** On *Normal Amyl Alcohol*, or *Normal Butyl Carbinol*,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , see 1st Suppl. pp. 106, 1137, and *Chem. Soc. J.* [2] ix. 1033.

*Isoamyl Alcohol*, or *Isobutyl Carbinol*,  $\text{CH}_3\text{CH}(\text{CH}_3)_2\text{CH}_2\text{OH}$ .—This alcohol, prepared by fractional distillation of beet fusel-oil, and carefully purified by means of the ordinary dehydrating agents, was found by Pierre a. Puchot (*Bull. Soc. Chim.* [2] ix. 1033) to exhibit the following physical properties:—\*

Boiling point, 130–130.1° under normal pressure. Index of refraction for the middle orange ray = 1.411. Rotation of a polarised ray (what colour?) in a tube 20 cm. long = 8.5° to 8.9° to the left. Sp. gr. determined directly at 0°, at other temperatures by calculation from the rate of expansion:

Temperature	0°	25°	50°	75°	100°	125°
Sp. gr.	0.826	0.808	0.780	0.768	0.746	0.720.

In a recent communication (*Compt. rend.* lxxvi. 1332) the same chemists give the following determinations of the densities, boiling points, and rotatory powers of several amyl compounds:—

	Density at 0°.	Boiling point.	Rotation in a tube 20 cm. long.
Amyl Alcohol (anhydrous) . . . . .	0.8255	130°	—8.5°
" " with 6 p.c. water . . . . .	—	—	—11°
" Valerate . . . . .	0.874	190°	+40°
" Butyrate . . . . .	0.8769	170.3°	+8.5°
Butyl Valerate . . . . .	0.8884	173.4°	+3°
Propyl " . . . . .	0.8862	157°	+0°
Ethyl " . . . . .	0.886	135.5°	+12.5°
Methyl " . . . . .	0.9005	117.5°	+8.5°
Valeric Acid . . . . .	0.947	178°	+5°
" Aldehyde (puro) . . . . .	0.8200	92.5°	+6°
" " (crude) . . . . .	—	—	+18°

They state that, in the course of their experiments, they have never met with optically inactive amyl alcohol; but they say nothing about the means which they adopted for obtaining it. Some of the discrepancies between their own determinations of the optical rotatory power of amyl-compounds and those made by other

\* These determinations agree nearly with those of other chemists, excepting as regards the optical rotatory power (see l. 203 and 1st Suppl. 107). Nevertheless, Messrs. Pierre a. Puchot appear to think that their own investigations are the first which have afforded satisfactory evidence of the existence of fermentation amyl alcohol, and of the corresponding propyl and butyl alcohol, as distinct chemical species. Moreover, they designate these alcohols as 'Normal Alcohols' (!)

observers are exactly such as might be expected to arise if the amyl compounds on which they experimented were mixtures of active and inactive compounds. Thus Pedler found that active valeric acid turns the plane of polarisation  $43^\circ$  to the right in a tube 50 cm. long, which is equivalent to a rotation of  $17\cdot2^\circ$  in a tube 20 cm. long; and Erlonmeyer a. Hell (*Ann. Ch. Pharm.* clx. 257) found a somewhat higher value: namely,  $48\cdot7^\circ$  for 50 cm., or  $19\cdot5^\circ$  for 20 cm., whereas Pierre a. Puchot find only  $5^\circ$ . On the other hand, the rotation which the latter assign to amyl alcohol, namely,  $8\cdot5^\circ$  for 20 cm., is rather higher than that given by Pedler, who obtained a rotation of  $17^\circ$  for 50 cm., or  $6\cdot8^\circ$  for 20 cm.

The most remarkable result of Pierre a. Puchot's experiments is, that amyl alcohol containing 6 p.c. water has a rotatory power ( $-11^\circ$ ) greater than that of the anhydrous alcohol ( $-8\cdot5^\circ$ ).

The numbers in the preceding table show also that isomeric compounds exhibit, in some instances at least, different optical rotatory powers: e.g. amyl butyrate ( $8\cdot5^\circ$ ) and butyl valerate ( $3^\circ$ ); also valeric aldehyde ( $6^\circ$ ) and amyl valerate ( $40^\circ$ ). In the latter case, however, the two compounds are polymeric, not merely isomeric.

According to Popoff (*Dent. Chem. Ges. Ber.* vi. 560), commercial amyl alcohol yields by fractional distillation a portion having a stronger rotatory power than the original liquid.

**AMYL HYDRIDE**, *Pentane* or *Quintane*,  $C^5H^{12}$ .—This hydrocarbon admits of three modifications, viz. :—

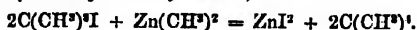
- (1)  $CH^3-CH^2-CH^2-CH^2-CH^3$
- (2)  $\begin{array}{c} H^3C \\ H^3C \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} CH-CH^2-CH^3$
- (3)  $C(CH^3)_4$ .

The first, or normal pentane, is contained in the light oils from Cannel and Boghead tar, and in large quantities in Pennsylvanian petroleum; it may be separated by fractional distillation, and boils at  $37^\circ-39^\circ$ . On passing chlorine into its vapour at the boiling heat, two *pentyl* or *amyl chlorides*,  $C^5H^{11}Cl$ , are obtained, one boiling at  $95^\circ-100^\circ$ , the other, which is the chief product, at  $100^\circ-102^\circ$ . These chlorides, decomposed with potassium acetate, yield *pentene* or *amylene*,  $C^5H^{10}$ , boiling at  $39^\circ-40^\circ$ , and two *acetic ethers* boiling between  $135^\circ$  and  $140^\circ$ ; and these ethers, decomposed by potash, yield normal primary *amyl alcohol*, boiling at  $134^\circ-137^\circ$ , and converted by oxidation into normal valeric acid, together with a secondary amyl alcohol: viz.

*methyl-propyl carbinol*  $\left. \begin{array}{c} CH^3 \\ C^5H^7 \end{array} \right\} CH\cdot OH$ , which yields by oxidation methyl-propyl ketone (Schlorlemmer, *Phil. Trans.* 1872, 111; *Chem. Soc. J.* [2] x. 1085).

The second modification, or isopentane, is obtained by dehydration of ordinary amyl alcohol; or by heating ordinary amyl iodide with water and zinc (1st *Suppl.* 115).

The third modification, or tetramethyl-methane,  $C(CH^3)_4$ , has lately been obtained by Lwow (*Zeitschr. f. Chem.* [2] vi. 520) by the action of zinc-methyl on tertiary butyl iodide (trimethyl-carbinyl iodide):

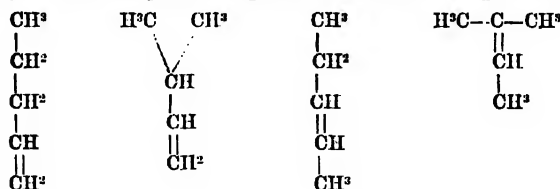


The zinc-methyl must be added to the tertiary iodide by drops. The action goes on without application of heat, and the escaping gas must be washed with dilute hydrochloric acid and received in strong, well-cooled alcohol. On diluting the saturated alcoholic solution with water, the gas is given off and may be condensed to a liquid in a well-cooled receiver. To remove adhering hydrocarbons it is treated first with bromine, then with sodium at  $100^\circ$  in a sealed tube. The quantity of the pure product obtained is nearly that required by theory. It might, perhaps, also be prepared by the action of zinc-methyl on dichloropropane,  $CH^3-CCl^2-CH^3$ .

Tetramethyl-methane is a colourless mobile liquid, which boils constantly at  $9\cdot5^\circ$  and solidifies at  $-20^\circ$  to crystals resembling sublimed sal-ammoniac. It is remarkable that other highly-methylated compounds (as trimethyl-carbinol, methyl oxalate, durenne, &c.) are likewise crystalline.

**AMYLENE**,  $C^5H^{10}$ .—This hydrocarbon, like the other olefines, might be represented as a molecule in which each carbon-atom is linked to its neighbours by only one unit of affinity, and consequently two units of affinity are unsaturated (see 1st *Suppl.* pp. 117, 718). It is, however, more in accordance with the known relations of these bodies to represent them, in the free state, as saturated molecules having two of their carbon-atoms linked together by two units of affinity, and to suppose that, when they come in contact with chlorine, bromine, &c., this double linking is broken up, the molecule then becoming bivalent, and capable of taking up  $Cl^2$ ,  $Br^2$ ,  $O$ , &c. On this view, the olefines will exhibit isomeric modifications, accordingly as the double

linking of the carbon-atoms takes place in the middle or towards the end of the chain. Amylene, for example, is susceptible of the four following modifications:—



The first of these is the amyleno corresponding to normal amylic alcohol, and probably identical with Wurtz's ethyl-allyl. The second is ordinary amyleno obtained from the amylic alcohol of fermentation. The fourth is obtained from tertiary amyl alcohol or dimethyl-ethyl carbinol,  $\text{C}(\text{CH}_3)_2(\text{C}^2\text{H}_5)\text{OH}$ , by the action of very strong alcoholic potash. It boils at  $35^\circ$ , unites with bromine, and with hydriodic acid when heated with the fuming acid to  $100^\circ$ , forming dimethyl-carbinyl iodide,  $\text{C}(\text{CH}_3)_2(\text{C}^2\text{H}_5)\text{I}$ , which is converted into tertiary amyl alcohol by treatment with silver oxide and water (Ermolaïen, *Zeitschr. f. Chem.* [2] vii. 275). The third is not positively known, but is perhaps identical with an amyleno boiling at  $25^\circ$ , which Flavitzky, has lately obtained by treating ordinary amyl iodide with concentrated alcoholic potash (*Ann. Ch. Pharm.* elxix. 205.)

**Conversion of Amylene into an Amyl Alcohol by Sulphuric Acid.**—According to Berthelot (*Ann. Ch. Pharm.* cxx. 71), small quantities of amyleno hydrate (secondary amyl alcohol) are formed by the action of sulphuric acid upon amyleno. Erlenmeyer (*Zeitschr. f. Chem.* 1865, 362) contradicts this statement, asserting that nothing but diamyleno is produced by this reaction. Flavitzky, however (*Ann. Ch. Pharm.* clxv. 157), found that when a stream of carbon dioxide charged with amyleno vapour was passed into a mixture of 2 parts sulphuric acid and one of water in an apparatus arranged so as to carry on the process continuously, part of the amyleno was converted into diamyleno, while the rest dissolved, forming a solution from which, on addition of water, an alcohol was separated. This alcohol boiled between  $100^\circ$  and  $108^\circ$ , and more than half of it at  $102.4^\circ$ . No amyleno hydrate was separated from it even by repeated fractional distillation. By oxidation with chromic acid mixture, it yielded common acetone, but no methyl-isopropyl ketone, which is the normal product of the oxidation of amyleno-hydrate. From the boiling point of the alcohol, it probably contained dimethyl-ethyl carbinol (tertiary amyl alcohol), which might be formed if the amyleno contained isomeric modifications.

**Diamylene,  $\text{C}^4\text{H}^{10}$ .**—This hydrocarbon is most easily prepared by shaking together one volume of pure amyleno with two volumes of strong sulphuric acid and one volume of water in stoppered cylinders immersed in ice-cold water. From the product, which boils at  $150^\circ$ – $170^\circ$ , pure diamylene may be isolated by fractional distillation. It boils at  $150^\circ$ – $153^\circ$  under a pressure of 721 mm., and has a specific gravity of 0.8416 at  $0^\circ$ , and 0.8248 at  $20^\circ$ .

A solution of potassium dichromate in dilute sulphuric acid acts slowly on diamylene in the cold, more quickly on heating; the products consisting—besides carbonic and acetic acids—of a neutral and of an acid oil, which may be separated by means of caustic soda.

The acid liquid which volatilises with the steam, consists of amethenic acid, a weak acid isomeric with cinnanthylic acid (p. 56).

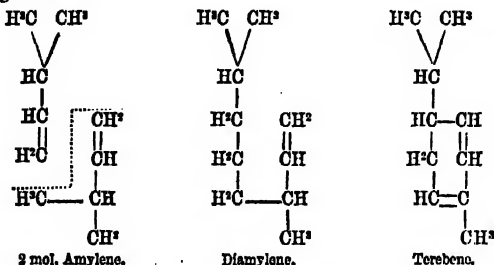
The neutral oil may be separated by fractional distillation into fractions boiling between  $140^\circ$  and  $210^\circ$ , and a residue which decomposes on further heating. The chief fraction, which boils between  $180^\circ$ – $190^\circ$ , has the composition of diamylene oxide,  $\text{C}^4\text{H}^{10}\text{O}$ . It is a light, mobile, colourless liquid, having a penetrating smell, like that of camphor. It easily reduces an ammoniacal silver solution, but does not combine with sodium bisulphite. It is the first product of the action of chromic acid upon diamylene, and yields by further oxidation, carbonic, acetic, and amethenic acids.

Phosphorus pentabromide does not act on the neutral oil in the cold; on heating, a quiet reaction sets in, hydrobromic acid and the compound  $\text{C}^4\text{H}^{10}\text{Br}$  being formed. Probably diamylene dibromide,  $\text{C}^4\text{H}^{10}\text{Br}_2$ , is first formed, a compound which easily decomposes even at ordinary temperatures (W. v. Schneider, *Ann. Ch. Pharm.* clvii. 185).

Diamylene unites with bromine as readily as amyleno does, and must therefore be supposed to have two of its carbon-atoms linked together by two units of affinity. The same view of its constitution affords an insight into the mode of its further condensation to triamyleno and tetramyleno, and of the formation of rutyleno,  $\text{C}^6\text{H}^{14}$ .

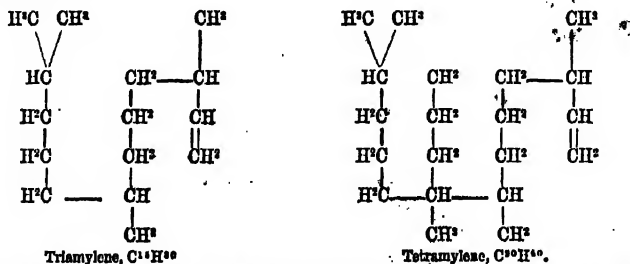


and terebene,  $C^{10}H^{16}$ , by abstraction of 2 and 4 atoms hydrogen respectively from diamylene. The transition from amylene to diamylene and terebene may be represented by the following formulae:—



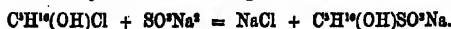
In terebene we see the closed ring of the benzene molecule; consequently, a further abstraction of  $H^{\circ}$  will give the molecule  $C^{10}H^{14}$ , homologous with benzene—in fact, isopropyl-methyl-benzene, which is one of the modifications of cymene; and this transformation has actually been effected. (See CYMENE and TEREBENE.)

The condensation of diamylene to triamylene and tetramylene may be represented as follows:—



Respecting v. Schneider's views of the constitution of diamylene, see *Ann. Ch. Pharm.* clvii. 185; *Chem. Soc. J.* [2] ix. 217.

**AMYL-ISETHIONIC, or OXYAMYL-SULPHONIC ACID.**  $C^8H^{14}SO^4 = C^8H^{13}(OH)SO^3H$ . (F. A. Falk, *J. pr. Chem.* [2] ii. 272).—This acid is formed by the action of amylene-chlorhydrin on sodium sulphite:



The two bodies are enclosed in a glass tube together with a little water, and heated to  $120^{\circ}$ ; the undecomposed amylene-chlorhydrin is then removed by distillation; the aqueous solution is mixed with the requisite quantity of sulphuric acid; the sodium sulphate precipitated by alcohol; the alcohol evaporated; and the residue freed, first from chlorine by silver sulphate, then from silver by hydrogen sulphide; lastly, the solution is saturated with baryta, and the barium salt decomposed by copper sulphate. The cupric salt thus formed is the most easily crystallisable of all the amyl-isethionates; its solution, decomposed by hydrogen sulphide, yields amyl-isethionic acid, which, however, cannot be obtained in the pure state, as the solution is decomposed by evaporation.

The metallic amylisethionates are more stable, their solutions not being decomposed by boiling. At higher temperatures, however, they decompose the copper salt a little above  $100^{\circ}$ . They are all very soluble and difficult to crystallise.

The sodium salt  $C^8H^{13}(OH)SO^3Na$  forms thin, white, very deliquescent laminae. The ammonium salt dries up over sulphuric acid to an amorphous mass. The calcium salt  $[C^8H^{13}(OH)SO^3]_2Ca$  crystallises in thin, soft, very soluble laminae; so likewise does the barium salt  $[C^8H^{13}(OH)SO^3]_2Ba$ , which decomposes at  $130^{\circ}$  with formation of barium sulphate. The copper salt  $(C^8H^{13}(OH)SO^3)_2Cu + 2H_2O$  dissolves easily in water and in alcohol, and crystallises in thin, soft, pale blue laminae. The lead salt crystallises with difficulty; the silver salt is very decomposable.

According to E. Schwarz (*Deut. Chem. Ges. Ber.* iii. 691), amylisethionic acid, or an isomeric acid, is produced by the action of sulphuric anhydride on amyl alcohol.

2nd Sup.

F

The anhydride is pressed into a glass tube 3 or 4 inches long and 2 lines wide, and this tube is introduced into a wider one containing cooled amyl alcohol. As soon as all the anhydride is dissolved, the solution is diluted with water, boiled for some hours, saturated with barium carbonate, filtered, concentrated, mixed with alcohol, again filtered, then left over oil of vitriol, and the hygroscopic crystalline mass which remains is purified by recrystallisation from dilute alcohol. The barium salt thus obtained forms distinct crystals easily soluble in water and in alcohol, and swelling up strongly when heated. The aqueous solution does not deposit barium sulphate when boiled.

**AMYL-PHOSPHOPLATINOUS ETHER.** See PHOSPHOPLATINOUS COMPOUNDS under PLATINUM.

**AMYL-PROPARGYLIC ETHERS.** See PROPARGYLIC ETHERS.

**ANALYSIS.** Application of Sulphuretted Hydrogen reactions to Analysis in the dry way (J. Landauer, *Deut. Chem. Ges. Ber.* v. 406).

Characteristic reactions may be obtained by heating the borax bead in which a metallic salt is dissolved, with sodium thiosulphate; but this method has the disadvantage of not being applicable to volatile metals like arsenic and mercury, besides that the production of liver of sulphur causes uncertainty by colouring the bead. Instead, therefore, of proceeding in this way, it is better to heat the substance with the thiosulphate in a test-tube. If the water of crystallisation of the reagent has not been previously expelled, the tube must be held horizontally to prevent the water running back and breaking it.

The annexed table shows that nearly all metallic compounds may be thus identified by means of the sulphide-reactions, aided by those with the ordinary borax bead.

Metallic oxide	With $\text{Na}_2\text{S}_2\text{O}_3$	Cold borax bead	
		In oxidising flame	In reducing flame
Antimony oxide	Red . . . .	Colourless . . . .	Grey to colourless.
Arsenious acid	Yellow . . . .		
Lead oxide	Black . . . .	Colourless . . . .	Grey to colourless.
Chromium oxide	Green . . . .	Yellowish-green . .	Emerald green.
Iron oxide	Black . . . .	Yellow . . . .	Bottle green.
Gold oxide	Black . . . .	Reduced without being dissolved.	Reduced without being dissolved.
Cadmium oxide	Yellow . . . .	Colourless . . . .	Grey to colourless.
Cobaltous oxide	Black . . . .	Blue . . . .	Blue.
Cuprous oxide	Black . . . .	Blue . . . .	Brownish-red (turbid).
Manganese oxide	Bright green . .	Violet . . . .	Colourless.
Molybdic acid	Brown . . . .	Colourless . . . .	Brown.
Nickel oxide	Black . . . .	Reddish-brown . . .	Grey to colourless.
Platinum oxide	Black . . . .	Reduced without being dissolved.	Reduced without being dissolved.
Mercury oxide	Black . . . .		
Silver oxide	Black . . . .	Colourless . . . .	Grey to colourless.
Uranium oxide	Black . . . .	Yellow . . . .	Bottle-green.
Bismuth oxide	Black . . . .	Colourless . . . .	Grey to colourless.
Zinc oxide	White . . . .	Colourless . . . .	Grey to colourless.
Tin oxide	Brown . . . .	Colourless . . . .	Colourless.

*New Method of Quantitative Inorganic Analysis.*—H. Carmichael (*Zeitschr. anal. Chem.* x. 82; *Zeitschr. f. Chem.* [2] vi. 481) points out that the ordinary methods of quantitative analysis are affected by several sources of error, arising not so much from the nature of the processes employed, or from impurity in the reagents, as from the manipulations required, especially the decantation of liquids from one vessel to another,—the separation of a precipitate from the filter, the burning of the filter, and the estimation of the ash being also not unimportant sources of inaccuracy. From an examination of a large number of published analyses, he infers that when 100 parts of a substance are taken for analysis, the sum of the constituents actually found varies from 100.67 to 99.17, or by about 1.5 per cent., while analyses in which it varies from 102 to 97 per cent. are by no means uncommon. Moreover, it is for the most part impossible to say whether the excess or deficiency should be distributed amongst several of the constituents or falls on one only.

To avoid the sources of error above mentioned, Carmichael has devised the following apparatus:—

The apparatus represented in Fig. 2—one-fourth of its actual size—consists of a glass tube twice bent at right angles, and having at one end a funnel-shaped enlargement, the bottom of which is pierced with a number of small holes. The other arm fits into the T-shaped tube BCD, which is closed air-tight at B with a caoutchouc ring. This tube is fixed into the glass plate EF, and is likewise closed air-tight with a caoutchouc ring. The plate EF is covered with a so-called caoutchouc 'cap.' Between B and C is attached a side-tube, bent at right angles at D, so that the spring-clamp which closes the small caoutchouc bag at D may be easily handled.

The 'cap' and the ring B are thinly coated with grease. The edges of the beaker glasses may be easily ground on a plate of sandstone. When the whole is exactly fitted, the cover EF closes so completely that the beaker may be kept air-tight for 24 hours.

FIG. 2.

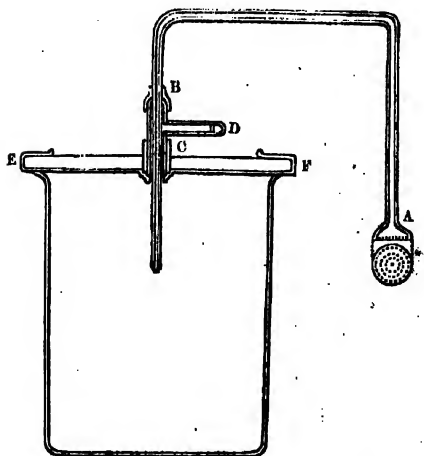
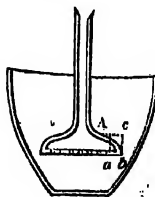


FIG. 3.



The filter-bulb A (Fig. 3), on the action of which the process mainly depends, is blown at the lower end of a tube 2 mm. in internal diameter; it is then flattened at the bottom, left to cool a little, and while the glass is kept in a scarcely soft state, pierced through the flattened surface with a fine white-hot steel wire. The holes must be close together, and must have a diameter not exceeding 0.7 mm. The width of the edges *a b* (Fig. 3) must be regulated according to the thickness of the paper with which the bulb is to be covered. For ordinary paper it must be 3 mm.; but it is better to use thin Swedish paper, and for this a width of 2 mm. is sufficient. The sieve thus formed is ground. The tube itself is bent in such a manner that the arm B is a little longer than A. The height *bc* must be small, so that the air which rises at the end of the filtration may drive all the liquid before it. For ordinary use, a diameter of 2.5 centimeters is sufficient. The number of holes required is in general about fifty; a smaller number will, however, suffice if they are connected together by narrow gutters etched out with hydrofluoric acid.

The apparatus is connected by means of a thick-walled caoutchouc tube with an exhausting apparatus, the exhaustion being made either with the lips or by a Sprengel pump, or an aspirator, according to circumstances.

To use the apparatus, the air is pumped out, whilst the end A is immersed in water; the rapid stream of water then washes out all impurities, and serves at the same time to rinse out the beaker. A disc of filter-paper of the same diameter as A is then pressed against the lower surface, and remains adhering to it, even when air is blown in again, and does not tear even under full atmospheric pressure. The vessel is now again exhausted, the disc of filter-paper having been previously immersed in the solution, but never to the bottom. When the solution has been filtered, the precipitate is washed a little; the apparatus, with the adhering precipitate, is removed; the remainder is washed into a tared crucible into which the bulb is also dipped, in order to wash it thoroughly. The air is then allowed to pass through the precipitate for some time, whereby the substance is almost completely dried, while gelatinous

precipitates become fissured and shrink together. The spring-clamp is then opened, so as to admit air into the beaker, and the filter-tube is removed both from the crucible and from the cover F E. When the operation has been properly performed, the disc of paper remains upon the precipitate. The upper surface of the bulb appears clean, and only a small ring of the substance remains adhering to the lower edge; this portion may likewise be removed by holding a small piece of filter-paper against the bulb with one hand, while with the other the tube is turned round, and the paper, with the small quantity of the precipitate adhering to it, is brought into the crucible.

The crucible is then covered and heated in an air-bath to  $105^{\circ}$ . At this temperature the precipitates dry very quickly, and there is no fear of subsequent spitting. The crucible is afterwards heated without its cover till the paper is burnt, and then raised to a red heat.

\* In most cases a bulb of the size above mentioned is sufficient; for gelatinous precipitates, however, like alumina and ferric hydrate, a bulb 3.5 centimeters in diameter is better. A small platinum dish, weighing about 28 grams, may also be advantageously substituted for the crucible.

One of the principal advantages ascribed to this method of analysis is the avoidance of loss in the washing and burning of a filter, and of error in estimating the weight of the ash; for as a filter 12 centimeters in diameter yields about 0.0005 gram of ash, the ash of the little discs of paper used in the preceding process cannot weigh more than 0.00002 grams, a quantity altogether inappreciable. Another advantage claimed for this process is the small quantity of substance required for the analysis, 2 milligrams being in fact sufficient, whereby a great saving of time is effected.

The same method may of course be applied to qualitative analysis (Carmichael).

*Filtration under pressure* may also be effected by means of the diminution of pressure which takes place on the cooling of a close space filled with steam. A cylinder of tin-plate which can be closed air-tight is connected by a glass tube having a glass stop-cock, with a bottle closed by a caoutchouc stopper, through which the neck of the funnel also passes. The cylinder is filled with steam by heating water contained in it, then closed, and brought into connection with the bottle which carries the funnel by opening the glass cock. As the cylinder cools, a partial vacuum is produced in the bottle, and the pressure of the external air forces the liquid through the filter (J. Oster, *Zeitschr. anal. Chem.* xi. 290).

To obviate the tearing of filters which sometimes takes place in filtering under pressure, C. Tiehborne (*Pharm. J. Trans.* 1871, 881) makes use of parchment-paper filters. These stand the pressure either with or without the help of a platinum cone. The only objection to them—namely, that they do not fit so close to the surface of the funnel as filters of ordinary paper do, and consequently permit the passage of air—may be obviated by first placing an ordinary filter in the funnel and the parchment-paper filter within it. For this purpose it is best to use paper converted into parchment-paper on one side only, the unaltered side being placed in contact with the ordinary filter.

To prepare such paper, pieces of Swedish filtering paper are carefully laid on a mixture of 2 parts pure strong sulphuric acid and 1 part distilled water, the mixture, if possible, being used ice-cold, and never while yet warm; care must be taken that every part of the surface comes in contact with the liquid. The paper must afterwards be quickly and thoroughly warmed.

*Earthenware Filters.*—These are made of very porous earthenware, compact enough, however, to prevent the most finely divided precipitates from running through. They are washed, before use, with hydrochloric acid and water, then dried—and if required for filtering under pressure—they are supported within a glass funnel by means of a piece of sheet caoutchouc passing over the edge of the latter (O. E. Munroe, *Dent. Ges. Chem. Ber.* iv. 279).

*Washing of Gelatinous Precipitates.*—To accelerate this process, which is long and tedious even with the air of a filter-pump, T. M. Chatard (*Zeitschr. anal. Chem.* xi. 299) mixes the liquids in which such precipitates are formed with a slight excess of the precipitant, and evaporates the whole to dryness, stirring the gelatinous mass with a glass rod till it forms a perfectly dry powder, which may then be easily washed on a filter. Examples given by Chatard of the analysis of potassium dichromate and ammonio-ferric sulphate, in which the precipitated chromic and ferric hydrates were thus treated, exhibit close agreement with the calculated results. Nevertheless, Fresenius thinks that the method cannot be applicable in all cases, inasmuch as the precipitates during evaporation to dryness may very easily enclose foreign matters, which will afterwards be very difficult to remove by washing; in fact, Chatard himself admits that such is the case with carbonate of cobalt.

*Calculation of Indirect Analyses.*—Let  $x + m$  and  $y + p$  be two compounds:  $x$  and  $y$  being the two constituents to be determined;  $m$  and  $p$  the quantities of the common

constituent whose sum =  $b$ , is known;  $a$  the sum of the weights of the two compounds: also let  $K$  denote the atomic weight of  $x$ ,  $N$  that of  $y$ ,  $O$  that of  $m$  and  $p$ ; then

$$x = \frac{K}{C} \cdot \frac{b(N+C) - aC}{N-K}$$

$$y = a - b - x.$$

The percentage of  $x$  contained in  $a$  is:

$$\frac{100K}{aC} \cdot \frac{b(N+C) - aC}{N-K} = \frac{100K}{C(N-K)} \cdot \frac{b(N+C) - aC}{a}$$

This shows at once that  $x = 0$  when

$$b(N+C) - aC = 0, \text{ or when}$$

$$\frac{b}{a} = \frac{C}{N+C}$$

If, therefore, in a substance regarded as a mixture of the chlorides of sodium and potassium, the quantity of chlorine found by experiment is to the total weight of the substance as 35.5 : 58.5, it follows that no potassium chloride can be present. The

fraction  $\frac{100K}{C(N-K)}$  is for the most part of considerable magnitude (in the determination of potassium and sodium chlorides, for example, it is 6.84). Errors in the estimation of  $a$  and  $b$  have a greater influence on the result in proportion as  $N-K$  is smaller; if  $N = K$ , the method is inapplicable (Casselmann, *Zeitschr. anal. Chem.* ix. 66); compare i. 224.

**Oxidation with Nitric Acid and Potassium Chlorate.**—F. H. Storer (*Sill. Am. J.* [2] xlviii. 190) recommends this mixture as preferable in most cases to all other oxidising agents commonly used in analysis. Chromic oxide, even after ignition, is easily and completely oxidised to chromic acid, by treating it with nitric acid to which potassium chlorate is gradually added; chrome-iron ore treated in the same manner does not dissolve completely, but the residue, tested by fusion with sodium-carbonate and nitro, is found to be quite free from chromium; metallic arsenic and arsenious acid are easily converted into arsenic acid; cinnabar is oxidised without separation of sulphur; the sulphur in potassium sulphocyanate, vulcanised caoutchouc, anthracite, bituminous coal, and pyrite, is completely oxidised and dissolved; and organic substances in general are so completely oxidised and decomposed, that this method of oxidation may perhaps afford an easy method of determining the carbon by passing the resulting carbon dioxide into baryta-water.

The oxidation in all cases is performed in a porcelain basin on the water-bath, and loss by spitting is prevented by placing in the basin an inverted funnel having its neck bent downwards.

**Oxidation with Nitric Acid in Organic Analysis** (i. 247).—For the oxidation of the elements of organic bodies other than carbon, hydrogen, and oxygen, Carus (*Deut. Chem. Ges. Ber.* iv. 697) now uses hydrogen nitrate of sp. gr. 1.5, which is easily prepared from the pure red commercial acid of sp. gr. 1.57 by gently heating in an open flask. The quantity used should be from one and a half times to twice that which is actually required for the oxidation according to the equation:



but the proportion of this quantity to the capacity of the tube should not exceed 4 grams to 50 cubic centimeters. The quantity of nitric acid required is in general very small, since, for example, 0.24 grams of mercaptan, which is one of those bodies which require the largest amount of oxygen, may be oxidised by 3.3, or at most 4.4 grams of nitric acid. The duration of the oxidation need never exceed an hour and a half, reckoning the first half hour for attaining the requisite temperature.

The temperature required for complete oxidation is very different for different bodies. Easily oxidable substances are decomposed at temperatures between 150° and 200°, compounds of the aromatic class at 250°–260°, while for derivatives of the sulphonic acids a temperature of 260° to 300° is required. Hard black wood-charcoal disappears very quickly at 250°–260°, traces of organic matter, however, remaining in the solution; at 300° it is easily and completely oxidised to carbon dioxide. English graphite disappears in two hours at 300°–330°, and is completely oxidised to carbon dioxide.

The oxidation is performed in sealed combustion-tubes 0.45 to 0.6 met. long and 0.013 met. wide. When it is complete the tube is opened, and cold water is slowly added to the greenish blue liquid, whereupon a considerable evolution of nitric oxide takes place.

The rest of the analysis is very simple. In the estimation of sulphur, the small quantity of nitric acid used renders the contamination of the barium sulphate with barium nitrate very small and easily removable. In the estimation of chlorine, bromine, and iodine, silver nitrate is immediately added to the contents of the tube, as in the mode of operating formerly described. Iodide of silver melts with the excess of nitrate into a yellow mass, and must be heated for two or three hours under the dilute liquid to separate the nitrate. The small quantity of nitric acid used precludes the formation of iodate.

*Use of Bromine in Analysis.*—P. Waage (*Zeitschr. anal. Chem.* x. 206) recommends the use of bromine as an oxidising agent in preference to nitric acid, chlorine, or a mixture of potassium chlorate and hydrochloric acid, for the following reasons:—The action of nitric acid is but feeble when the acid is used in a dilute state, and even when concentrated it oxidises sulphur but slowly. Most solutions used in analysis are rarely quite free from hydrochloric acid (chlorides), and the use of platinum vessels has, therefore, to be carefully avoided. Nitric acid, lastly, acts upon filter-paper, the nitrocellulose preventing the complete precipitation of certain metallic oxides. Potassium chlorate necessitates the employment of concentrated hydrochloric acid, and any undecomposed chlorate, especially in dilute solution, can only be removed by introducing into the solutions a large excess of free hydrochloric acid. Chlorine-water is a comparatively weak oxidising agent, as it contains only about one-half per cent. of chlorine; and the use of gaseous chlorine involves each time the generation of chlorine and the preparation of a chlorine apparatus. Waage recommends, therefore, the more frequent use of bromine, both in qualitative and quantitative analysis, either in the form of pure bromine, or dissolved in water, or in concentrated hydrochloric acid. Bromine water, obtained by shaking up bromine with cold water, contains from 2 to 3 per cent. of bromine; concentrated hydrochloric acid takes up about 13 per cent. Either of these three oxidising agents may be employed, according to the intensity of the oxidising power to be exerted. Excess of bromine can be very easily removed by heat. Bromine, moreover, is without action upon platinum vessels, either in alkaline or acid solutions, free nitric acid excepted, and does not act upon filter-paper when used in the form of bromine-water or dissolved in hydrochloric acid—a great desideratum, whenever precipitates have to be partly oxidised on the filter itself.

Bromine is a useful and powerful solvent for sulphur, magnetic pyrites, copper pyrites, arsenical pyrites, nickel glance, as well as for precipitated sulphides, for determining either the sulphur or the metals. Sulphur shaken up with bromine and water in the proportion of about 15 parts bromine to 1 part of sulphur is speedily converted into hydrobromic and sulphuric acids. The whole of the bromine is added at once, in order to avoid loss of sulphur in the shape of sulphur bromide. The pyrites need not be powdered very finely; the action of bromine being very violent, it is advisable to add first a little water to the pieces of pyrites, and then the bromine in small quantities at a time, and with repeated shaking.

Bromine-water may conveniently be used for removing sulphuretted hydrogen from solutions. Precipitated metallic sulphides must, for the most part, be removed from the filter by a fine jet of water from a wash-bottle, and the last traces treated on the filter by pouring a little bromine gas or bromine water into the funnel and covering it up with a watch-glass. The sulphides are rapidly oxidised and absorbed by the filter, and can then be washed out.

Bromine does not oxidise in ammoniacal solutions, but liberates nitrogen; ammonia may therefore be used with advantage for removing excess of bromine. The peroxides of nickel, cobalt, and manganese, e.g., are not precipitated by bromine from solutions containing ammoniacal salts. Ferrous, stannous, and mercurous salts, on the contrary, are readily oxidised by bromine in an acid solution in the presence of ammoniacal salts.

Commercial bromine cannot always be obtained pure, and should be redistilled, if necessary, without the intervention of caoutchouc.

*Sources of Error in Volumetric Analysis.*—Errors may arise in volumetric determinations from the contraction which takes place on mixing saline solutions with water, and from the fact that vessels do not deliver in a given time corresponding volumes of water and saline solution, but rather less of the latter, the exact amount depending to some extent upon the specific gravity of the solution. The first-named source of error may be obviated: first, by using as weak solutions as possible; secondly, by mixing the saline liquids thoroughly with the water before making quite up to the required bulk. The error caused by the adhesion of a saline liquid to the delivering vessel may be obviated by graduating it in terms of the particular solution to be employed (*Tatlock, Chem. News*, xxiii. 13).

*Volumetric Estimation of Sulphuric Acid, Baryta, Chlorine, Bromine, and Iodine.*—(Bohlig, *Arch. Pharm.* [2] cxlv. 118).—This method is based upon alkalimetric

principles. Alkaline sulphates are known to be partially decomposed, in contact with barium carbonate, into alkaline carbonates and barium sulphate. The decomposition is complete in presence of free carbonic anhydride; acid carbonates of the alkali-metals are left in solution, together with some acid barium carbonate, which can be removed by boiling. The solution is filtered, and the alkaline carbonate determined by means of a standard acid solution, and the amount of sulphuric acid or alkaline sulphate calculated from the amount of normal acid required.

Neutral chlorides, bromides, and iodides, more especially of the alkali-metals, are most readily decomposed by pure silver oxide into insoluble silver salts, leaving the alkali-metal in solution as hydrate (ammonia salts always excepted), which can then be determined as usual by standard acid.

Solutions containing sulphates of the heavy metals, of the earths or alkaline earths (lime), and free from acids whose presence would influence the method, viz., phosphoric, arsenic, oxalic, &c., are treated with a solution of potassium carbonate so as to precipitate the bases and leave about double or treble the amount of alkaline carbonate in solution. From 1 to  $1\frac{1}{2}$  gram of substance is operated upon in a flask. The solution is made up to 500 c.c., well shaken, and the precipitate allowed to subside. 50 c.c. are then filtered into a porcelain dish and heated to boiling, and standard acid (HCl) added to neutralisation. Another 100 c.c. are filtered, in like manner, into a strong quarter-litre flask, and diluted with about 100 c.c. of hot water; the requisite quantity of normal acid is then run in at once from a burette; the solution diluted to 250 c.c.; and about a gram of dry barium carbonate (free from alkali) added. The flask is next closed and the liquid well agitated. The decomposition of the alkaline sulphate is completed in a few minutes. The flask should be opened now and then to allow the carbonic anhydride to escape. Finally, about  $\frac{1}{2}$  gram of pulverised barium hydrate is added, the whole well shaken, and a portion of the rapidly clearing liquid tested qualitatively for barium and sulphuric acid. The result should be negative. 50 c.c. corresponding to 20 c.c. of the original solution are then filtered into a porcelain dish and standardised with normal acid (hydrochloric or sulphuric), and the quantity of sulphuric acid (sulphate) calculated as usual. The source of carbonic anhydride is thus placed in the liquid itself, provided the quantity of potassium carbonate be not too small. Molecular quantities of  $K_2SO_4 + 2K_2CO_3 + 2HCl + BaCO_3$ , when mixed with sufficient water, change into  $BaSO_4 + 2KHCO_3 + 2KCl$ , and it is therefore more than sufficient to add twice the quantity of potassium carbonate compared with the alkaline sulphate operated upon. Barium hydrate is added with the view of removing any carbonic anhydride left in the liquid after boiling, which would otherwise dissolve some of the excess of barium carbonate contained in the precipitate. Any barium hydrate not required to remove carbonic anhydride is acted upon by the hydro-potassic carbonate, but does not influence the final result.

Phosphoric and oxalic acids may be removed by means of calcium chloride, chromic acid by deoxidising agents, such as alcohol and hydrochloric acid. Böhlig recommends this method for estimating sulphuric acid volumetrically in ashes, crude soda, Stassfurt salts, &c.

Solutions containing baryta are estimated in like manner by precipitation as carbonate, and decomposition with potassium sulphate in a solution containing free carbonic acid. Chlorine is determined volumetrically in solutions by first precipitating any metallic chloride with potassium carbonate added in moderate excess. The filtrate is made up to 250 c.c. and the excess of potassium carbonate determined in 50 c.c. by means of a normal solution of hydrochloric acid. 125 c.c. of the solution are next treated with excess of silver oxide and made up to 250 c.c., well shaken (in the dark) and filtered. 100 c.c. of the filtrate are standardised with normal hydrochloric acid solution. The difference between the quantity of acid required in the last experiment and that of the former experiment, multiplied by 5, gives the amount of chlorine contained in the original solution. A portion of the filtrate should be tested for chlorine by means of mercurous nitrate.

The filtrate is obtained perfectly clear only in presence of potassium or sodium carbonate, and by employing argentic oxide free from argentous oxide. A few drops of pure potassium permanganate added to the argentic oxide suspended in water, prevent the formation of argentous oxide. The oxide to be employed for each experiment is filtered when required, and thoroughly washed.

Bromine and iodine are determined in like manner. The method has not, however, been yet applied to the estimation of mixtures of the halogen salts; but it has been observed that potassium iodide, when boiled with potassium permanganate, is completely oxidised into iodate. This facilitates the detection of small quantities of chlorine and bromine in presence of much iodide. The greater part of the iodate may be separated also by precipitation with barium nitrate before determining chlorine. The standard acid solutions employed contain not more than one-third of the acid

valent of hydrochloric or sulphuric acid per litre. The strength may be determined by means of pure potassium carbonate or ignited potassium sulphate.

An apparatus for the quantitative analysis and synthesis of gases and vapours, chiefly for lecture experiments, is described by E. Mulder (*Zeitschr. f. Chem.* [2] vii. 2).

An apparatus for gas-analysis, similar in principle to that of Frankland and Ward, but of simpler construction, is described by J. Parry (*Chem. News*, xxiv. 282).

**ANETHOL.**  $C^6H^4O$ .—This compound is the methylic ether of anol or allyl-phenol  $C^6H^4\left\{\begin{smallmatrix} OH \\ C^6H^3 \end{smallmatrix}\right.$  (1st Suppl. 175). It has a specific gravity of 0.9877, and its index of refraction is 1.5430 for the line A, and 1.6129 for H (Gladstone, *Chem. Soc. J.* [2] viii. 147). Treated with phosphorus pentachloride, it yields phosphorus trichloride and chloranethyloxy,  $C^6H^4OClO$ :



Chloranethol is a light yellow liquid, which solidifies at low temperatures, melts at  $6^\circ$ , boils at  $258^\circ$ , and has a sp. gr. of 1.1254 at  $0^\circ$ . The chlorine-atom is very intimately combined. By heating with alcoholic potash, HCl is removed, and a body is formed which boils at about  $240^\circ$ , and probably has the composition  $C^6H^4O$ . Chloranethol is oxidised by silver acetate at  $260^\circ$ , with formation of anisic acid.

Sodium amalgam scarcely acts either upon anethol or upon its addition-product with hydrogen chloride, only a small quantity of a substance being formed, which boils at  $220^\circ$ – $224^\circ$ , and appears to contain the compound  $C^6H^4O$ .

With 1 mol. bromine, anethol forms an addition-product, anethol dibromide,  $C^6H^4OBr_2$ , which crystallises in small needles, insoluble in water, soluble in ether and in chloroform, melting at  $65^\circ$  (Ladenburg, *Ann. Ch. Pharm. Suppl.* viii. 87).

**ANGELINE.** An alkaloid contained, according to Peckolt (*Vierteljahrsschrift pr. Pharm.* xviii. 444), in *Ferreira spectabilis* (known in Brazil, where it is indigenous, as *Angelin-pedra*), in a reddish resinous mass deposited between the bark and the wood. This mass, which in some trees amounts to 20 or 30 pounds, has the following composition:—

Chestnut-brown resin . . . . .	3.64
Extractive matter . . . . .	5.45
Angeline . . . . .	86.84
Angelinic acid (cryst. organic acid) . . . . .	1.28
Acid potassium tartrate and chloride . . . . .	0.05
Red colouring matter . . . . .	0.42
Gum with inorganic salts and traces of sugar . . . . .	0.15
Moisture . . . . .	2.17

100.00

The angeline is extracted in the form of hydrochloride. Genth (*J. pr. Chem.* cxi. 116) regards it as impure ratanhine.

**ANHYDRIDES.** On the reaction of various anhydrides with phosphorus trichloride, see that compound, under PHOSPHORUS.

**ANHYDRITE.**  $CaSO^4$ .—This mineral often occurs associated with gypsum and rock-salt, in such a manner as to indicate that it is not a primary formation, but has been produced by dehydration of gypsum. That it can be produced in this manner, especially in presence of sodium chloride, has been shown by the experiments of Hoppe-Seyler and of G. Rose, both of whom find that crystallised gypsum, or selenite, heated to  $130^\circ$  in a saturated solution of sodium chloride, is converted into a white opaque mass made up of microscopic crystals of anhydrite. Rose also finds that crystals of selenite heated for a short time with solution of sodium chloride in a platinum dish are converted on the edges into fibrous anhydrite. Powdered gypsum similarly treated is converted into small prismatic crystals of anhydrite; and a saturated solution of gypsum mixed with an equal volume of concentrated salt solution, when evaporated, yields microscopic crystals of anhydrite. Pseudomorphs of anhydrite in the form of gypsum are found at Sulz on the Neckar (G. Rose, *Jahrbuch Mineralogie*, 1871, 932).

W. Scherer (*Zeitschr. f. Chem.* v. 324) obtained crystals of anhydrite of sp. gr. 2.022 by evaporating a solution of burnt gypsum in very strong sulphuric acid. 100 parts



sulphuric acid of sp. gr. 1.82 dissolve at ordinary temperatures 1.992 parts of artificial and 1.958 of natural anhydrite.

Anhydrite from the Schäfferotz mine, near Werfen, where it occurs in a bed two feet thick, accompanied by gypsum, has a specific gravity of 2.978, and contains 40.96 p.c.  $\text{CaO}$ , 58.44  $\text{SO}_2$ , and 0.42  $\text{Fe}_2\text{O}_3$  (Zepharovich, *Jahrbuch d. geolog. Reichsanstalt*, ii. 378).

Anhydrite nodules (A) coated with gypsum (B), varying in size from that of a hazel-nut to that of a walnut, occur in the rock-salt of Vizakna in Transylvania:—

	CaO	SO <sup>a</sup>	H <sup>2</sup> O	Cl	Sp. gr.
A 39.37		54.73	1.20	0.72	2.901
B 31.99		46.93	16.05	1.50	2.423

The proximate composition of the nucleus and crust is—

Gypsum	5.71	76.44
Anhydrite	91.09	17.28
Sodium chloride	1.20	2.48
Excess of sulphuric acid	0.50	1.25

(Posepny, *Verh. geolog. Reichsanstalt*, 1869, 140).

#### ANILINE. See PHENYLAMINES.

**ANILINE COLOURS.** *Preparation without the use of Arsenic.*—All attempts hitherto made to produce aniline-red on the manufacturing scale without the use of arsenic, or to dispose economically of the arsenical residues, have proved unsuccessful. As, however, only a small proportion, not more than one-tenth of the rosaniline manufactured is used for dyeing, the greater part being consumed in the preparation of other aniline colours, it is very desirable that these latter should be obtained from other sources.

The process of Girard and De Laire for obtaining diphenylamine blue by heating diphenylamine with carbon trichloride is said to have proved commercially successful, and the same chemists have obtained, without the use of arsenic, the violet colours usually produced by acting on rosaniline with alcoholic iodides, the process consisting in oxidising the secondary monamines, methyl-aniline, methyl-toluidine, &c. They expect also to be able to produce a green colour in a similar way (*Compt. rend. lxxiv.* 1556).

*New Sources of Methyl- and Ethyl-aniline.*—In the process of manufacturing the Hofmann violet by the action of ethylic or methylic iodide upon rosaniline or one of its salts, there is always produced a considerable quantity of a dark-coloured resinous substance, which has received the name of 'Hofmann gum.' When the water is expelled from this gum by fusion, and the residue is submitted to destructive distillation at a higher temperature, it yields nearly pure methylaniline or ethylaniline, according as the gum has been derived from the methylic or ethylic iodide. The methylaniline is an oily body boiling at 200°, and forming permanently liquid compounds with acids. With arsenic acid it furnishes a reddish violet dye, which may be converted into the bluer shades by the Hofmann process. The ethylaniline boils at 205°–210°. Both these oils, when heated with rosolic acid or rosaniline, do not yield Girard's blue, but change slightly towards violet and then suddenly become decolorised (Spiller, *Proc. Roy. Soc.* xxi. 204).

*Tinctorial Power of Aniline Colours.*—A solution of 1 part of a rosaniline salt in a million parts of water containing acetic acid still exhibits a deep crimson colour. A skein of silk moistened with dilute acetic acid is instantly dyed a fine red by this solution. In a solution of 1 part rosaniline salt in 25 million parts of water, the red tint is still very perceptible, and silk dropped into it is dyed light red in a quarter of an hour. With a solution of 1 part of salt in 100 million parts of water, the limit is attained at which the colour is still visible. Thin films of such a solution appear quite colourless, the tint being perceptible only in thick layers (about 18 inches). A silk thread immersed in such a solution acquires in 24 hours a red colour, deeper than that of the liquid. This phenomenon points to a state of movement among the molecules, in consequence of which, currents are established in the apparently motionless liquid, and in this manner the particles of the liquid are carried successively to the surface of the thread. The colours of aniline violet and iodine-green are still visible in solutions of 100 millions, and fix the corresponding colour faintly on fabrics after 24 hours' time; but they are not so well adapted as the red for these limit experiments, as much as violet and green in the dilute state approach more nearly to the colour seen on looking through considerable thicknesses of pure water (*A. N. H. Deut. Chem. Ges. Ber.* iii. 661).

**Complementary Colours of Aniline Dyes.**—Rosaniline salts exhibit by transmitted light a deep purple-red; their larger crystals reflect a splendid cantharides-green—the two tints coinciding, according to Dove's experiments (*Deut. Chem. Ges. Ber.* iii. 660), with the complementary colours of a plate of gypsum having a difference of  $\frac{1}{4}$  of a wave-length in polarised light. A concentrated solution of iodine-green in alcohol left to evaporate on a glass dish leaves a homogeneous transparent varnish which transmits a splendid green light, and exhibits by reflected light a highly characteristic red copper lustre, which comes out with peculiar brilliancy on friction: these two colours coincide, according to Dove, with those of a gypsum lamina having a difference of  $\frac{1}{2}$  of a wave-length. On warming the glass plate, the green passes into violet, and the reflected tint becomes brass-yellow, corresponding, according to Dove, with a difference of  $\frac{3}{4}$  to  $\frac{1}{2}$  of a wave-length (*Hofmann, Deut. Chem. Ges. Ber.* iii. 660).

**Valuation of Aniline Colours.**—Two-tenths of a gram of the particular colour in a pure state is to be dissolved in 100 c.c. of collodion, and the solution poured over a clean glass plate laid at an angle of  $60^\circ$ . An equal weight of the material to be valued is to be dissolved in 50 c.c. of the same collodion and a drop or two poured on another glass plate at the same angle. If after drying the two films have an equal depth of colour, the material obviously contains 50 per cent. of pure colouring matter; if, however, the second film be darker, the solution from which it proceeds is to be gradually let down, by addition of measured quantities of the collodion, till it gives a film of the same depth of tint as the standard. The number of cubic centimeters of collodion employed in all expresses the percentage of pure colouring matter (*A. Müller, Dingl. polyt. J.* ccii. 458).

**Adulteration of Aniline Colours.**—Bronze powder and crystals of sugar are frequently used for this purpose, especially for adulterating fuchsine. Bronze powder is easily detected by its insolubility; sugar by spreading the sample on a sheet of white paper and examining it with a lens. The pure crystals of fuchsine are recognised by their acicular forms and by appearing red (by transmitted light) at the edges only. The appearance of more rounded crystals, especially of such as have a garnet or faint amethyst-red tint is suspicious. Such crystals should be picked out and heated on the point of a spatula, when, if they consist of sugar, the characteristic odour of caramel will be given off (*W. F. Gintl, Dingl. polyt. J.* cciv. 163).

On the constitution of aniline colours, see Zulkowsky (*Wien. Akad. Ber.* lix. [2] p. 133; *Jahresb.* 1869, p. 698).

**Reduction (Enleavage) of Aniline Colours.**—This may be effected by zinc-dust, as follows: 100 parts of zinc-dust are very intimately mixed with 50 parts of a gum solution of 20 Bm. and 20 parts of a solution of sodium thiosulphate of sp. gr. 26° Bm. are added. The dyed fabrics are printed with this mixture, then dried and steamed, and lastly washed with very weak hydrochloric acid.

**Aniline Black.** The various kinds of oil which are used for the manufacture of aniline black never consist of pure aniline, their composition varying with their boiling points and specific gravities. Those anilines ordinarily consist of from—(a) 60 to 65 per cent. of a product boiling between  $180^\circ$  and  $185^\circ$ , which may be regarded as almost pure aniline. (b) 18 to 22 per cent. of a product boiling from  $185^\circ$  to  $192^\circ$ , which may be considered to be a mixture of aniline and toluidine. (c) 8 per cent. of a product boiling from  $192^\circ$  to  $198^\circ$ , which is toluidine; and (d) 4 to 6 per cent. of other products, as xylidine, cumidine, &c.

The specific gravities of the above fractions are about as follow:—

(a) From $2.75^\circ$ to $3.4^\circ$ , Baumé.	
(b) " $1.6^\circ$ " $2.1^\circ$ "	Pure aniline of Couper, $3.5^\circ$ , Baumé.
(c) " $0.6^\circ$ " $1^\circ$ "	Ordinary toluidine, $0.88^\circ$ "
(d) about $0.5^\circ$	Pseudotoluidine, $0.50^\circ$ "

Pure aniline oil of Couper, as also all products boiling from  $180^\circ$  to  $185^\circ$ , yield beautiful brilliant blacks. Pseudotoluidine, and the products boiling from  $185^\circ$  to  $192^\circ$ , yielded a black with a blue shade. Ordinary toluidine of Couper, and the products boiling above  $192^\circ$ , gave unsatisfactory shades between brown and black.

It appears then, that in testing the quality of aniline for the production of black dyes, the specific gravity affords important indications. For quick determinations, Baumé's areometer may be used with advantage.

Aniline oil of sp. gr.  $2^\circ$  to  $3\frac{1}{2}^\circ$  B., if not wilfully adulterated, will yield a good black at more than  $3\frac{1}{2}^\circ$  B. it generally contains nitro-benzene; and at less than  $2^\circ$  B. it contains too much toluidine, which is decidedly injurious.

Fractional distillation gives a still more accurate idea of the value of the oil, the quantity coming over between 180° and 190° being taken as the measure.

The value of a given sample of aniline oil may also be estimated by comparing the quantity of it required to produce a certain quantity of black dye with the quantity of pure Coupler's aniline required for the same purpose (C. Hartmann, *Dingl. polyt. J.* ccii. 389).

A. Müller (*ibid.* cci. 363) prepares an oxidised aniline-black by dissolving 20 grams of potassium chlorate, 40 grams of copper sulphate, 16 grams of ammonium chloride, and 40 grams of aniline hydrochloride in 500 c.c. water, warming the liquid to about 60°, and then removing it from the water-bath. In about three minutes the solution froths up and gives off vapours which strongly attack the breathing organs. If the mass does not become quite black after the lapse of a few hours, it is again heated to 60°, and then exposed in an open place for a day or two, and afterwards carefully washed out till no salts are to be found in the filtrate. For use in printing, the black paste is mixed with a somewhat large quantity of albumin, and the goods after printing are strongly steamed. The paste can be pressed into moulds and used as a substitute for Indian ink. When thoroughly dried *in vacuo* it appears as a black powder, which contains 39.28 p.c. C, 7.41 H, and 7.41 N, agreeing approximately with the formula  $C^{12}H^{11}N^{2}O^{11}$ , which requires 30.78 C, 3.86 H, and 7.72 N.

According to H. Rheineck (*Dingl. polyt. J.* cciii. 485), an equally good black may be obtained without the use of sal-ammoniac. On mixing equal weights of aniline (containing toluidine), hydrochloric acid and potassium chlorate with a minute quantity of cupric chloride and a sufficient quantity of water, and leaving the mixture to evaporate spontaneously, a black powder was obtained, which when washed with water, burnt without residue. 100 parts of aniline thus treated yielded 1206 parts of aniline black. With pure aniline only 114.8 p.c. of black was obtained, and it was of very poor quality.

Rheineck finds that aniline-black is a powerful base, and proposes to designate it by the name of *Nigraniline*. When any fabric is immersed in the mixture above described, it first acquires a dark green colour, but after treatment with alkalis this colour changes to dark violet. The dark green body is the hydrochloride of the aniline black, and the dark violet body the free base. With soda or ammonia, 8.9 p.c. of hydrochloric acid can be extracted: therefore the molecular weight of the hydrochloride is about  $100 \times \frac{36.5}{8.9} = 410$ , and that of the free base 373.5. This base has the power

of abstracting the acids from the salts of aniline. A small piece of cotton, on which a very thin layer of the dark violet colour is brought, is immediately coloured green by aniline hydrochloride, even in presence of excess of aniline. A piece of cotton moderately coloured with aniline black is a good test for the presence of free acids or alkalis, and the same piece may be used several times without losing its colour. When turned green by an acid, it should be well washed with distilled water, when it will be found to change quickly to violet, in presence of an alkaline solution as weak as that found in spring water. The black-green body (not previously treated with alkalis) treated with concentrated sulphuric acid, gives off hydrochloric acid gas, and yields a violet solution, which on evaporation leaves a black-green residue, doubtless the sulphate.

*Action of various Metals in the Production of Aniline Black.*—The presence of copper in some form has hitherto been regarded as essential to the formation of aniline-black; indeed, all black colours believed to be formed in the ordinary processes without the aid of copper are said to owe their formation to its presence in the vessels in which they are prepared, or in the rollers employed in printing. Mere traces of copper are sufficient to produce a black colour, but the presence of this metal in some quantity is generally regarded as indispensable. Cupric sulphate was first used, but for various reasons was subsequently replaced by the sulphide.

Lightfoot, however, finds that the copper in this preparation may be replaced by a few other metals. A mixture of basic aniline hydrochloride and ammonium chlorate, thickened with starch, was printed by a wooden roller on well bleached cotton, and whilst the fabric was still damp, the following metals were brought in contact with it and allowed to remain so for 15 minutes:—Copper, iron, vanadium, uranium, nickel, lead, zinc, antimony, tin, manganese, chromium, bismuth, arsenic, titanium, tungsten, cadmium, tellurium, molybdenum, mercury, silver, gold, platinum, palladium, rhodium, iridium, aluminium, osmium, cobalt, ruthenium, thallium, magnesium, lithium, lanthanum, didymium, erbium, yttrium, selenium, tantalum, niobium. After this, the fabric was hung up in a warm and damp place for 12 hours, and then passed through an alkaline bath. The result was that the best black was obtained with vanadium, next with copper, then with uranium, and lastly with iron. All other metals give either very little colour, or none at all. A sovereign and a shilling

previously found to have no effect, were shaken in a bag with some copper coins, and then placed in contact with the piece of cotton, when the sovereign produced a grey, and the shilling an almost black tint (*Dingl. polyt. J.* cciii. 483).

**Dyeing of Cotton Fabrics with Aniline-black** (*J. Persoz, Bull. Soc. Mtd. de Mulhouse*, xlii. 47; *Dingl. polyt. J.* cciv. 491).—In dyeing these fabrics black by immersion in a bath of potassium dichromate and an aniline salt, considerable difficulty has been experienced in regulating the strength of the solutions so as to produce a uniform tint. If the solutions are too dilute, no black is obtained; if they are too strong, it is precipitated in the bath instead of on the fabric: and if to retard the precipitation the solution is cooled to 0°, aniline chromate crystallises out and makes spots on the cloth; and when the influence of the low temperature is removed there is danger of the cloth taking fire in the neighbourhood of these spots from the reaction between the elements of the chromate and the organic matter.

These difficulties may be overcome by sprinkling the solutions, either successively or together, on the cloth, by means of a horizontal brush made to move quickly up and down, the cloth being tightly stretched and passed under it at a uniform rate. In working in this manner the production of the black cannot take place till the solutions are intimately mixed in the cloth and the latter is well soaked with the mixture.

The aniline salts best adapted for the purpose are the acid sulphates, nitrates, and hydrochlorides; \* neutral salts do not give a good result; neither can the acetate, oxalate, or any other organic salt be used. The acid sulphates give a reddish black, whilst the hydrochlorides and nitrates give a black with violet or blue lustre. A mixture of equal volumes of the disulphate and dihydrochloride gives very good results. The dichromate must be used in rather strong solution, not less than 80 grams to the litre.

The method above described gives first a dark green colour, which changes to pure black when the cloth is washed in water, and then passed through a hot soap-bath. By printing the cloth with resins or fats previous to dyeing, white patterns on a black ground may be obtained.

Lauth (*Moniteur scientifique*, xi. 600; *Bull. Soc. Chim.* [2] xix. 437) has invented a process for dyeing and printing all vegetable and animal substances with aniline-black. Cotton, linen, hemp, wood, &c., are first mordanted with a manganous salt, then passed through a bath of caustic soda, and afterwards treated with chloride of lime to peroxidise the precipitated manganous oxide. The mordanted fibre is then washed, and immersed in a bath of 1 litre of water, 50 grams of aniline, and 100 grams of hydrochloric, or 150 of sulphuric acid. The green colour at first produced is changed by treatment with alkalis or soap to a deep black, which may be further intensified by treatment with potassium dichromate or with salts of copper, chromium, or mercury, especially with a mixture of potassium chlorate, copper sulphate, and sal-ammoniac (1 gram of each to the litre). Lastly, the dyed material is washed with water and boiled with soap.

On wool, silk, leather, hair, feathers, ivory, &c., the precipitate of manganic oxide is produced by immersion in a solution of alkaline manganate or permanganate, the remainder of the process being the same as above described. By varying the concentration of the mordants and of the dye-bath to which also other bases, such as toluidine, cumidine, naphthylamine, may be added, grey-blue and brown-violet tints may be produced.

This process gives fine permanent blacks, but the mordanting is somewhat troublesome, and the black rubs off a little.

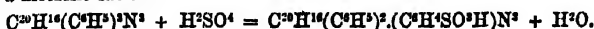
Gonin & Glanzmann (*Monats. sci.* xi. 302), employ the following mixture for printing a pure black on silk and wool:—1000 grams of gum-solution; 100 potassium chlorate; 100 sal-ammoniac; 250 aniline hydrochloride; 125 aniline nitrate of 50° Bm. If the thickening material be partly or wholly omitted, the mixture may be used for dyeing.

**Aniline Blue for Printing.** A blue paste for printing may be prepared by mixing 100 grams of starch with a litre of water, and adding to it while warm 40 grams of potassium chlorate, 3 to 4 grams of ferrous sulphate, and 10 grams of sal-ammoniac. The well-mixed paste, when quite cold, is mixed with 70 grams of aniline hydrochloride, or an equivalent quantity of the tartrate, and immediately used. The printed goods are oxidised, then passed through warm or faintly alkaline water, whereby the blue colour is developed (*Blumer-Zweefel, Dingl. polyt. J.* ccii. 103).

\* The recommendation of acid salts is contrary to the experience of Lightfoot, who used basic salts (*vide sup.*). As no copper salt is added in the process of Persoz, it is possible that the use of the free acid may be to take a trace of copper from the vessels, &c., with which the solutions come in contact.

**Sulphoacids of Aniline Blue.** (Bulk, *Dent. Chem. Ges. Ber.* v. 417.) Four different acids are obtained by the action of strong sulphuric acid on aniline blue, viz.:—

1. *Triphenylrosaniline-monosulphonic acid*,  $C^{20}H^{14}(C^6H^5)_3(C^6H^4SO^3H)N^3$ , is formed by dissolving triphenylrosaniline hydrochloride in strong sulphuric acid and heating the solution for five or six hours. On adding water, the sulpho-acid is obtained as a dark blue bulky precipitate, which, when dried at  $100^\circ$ , appears as small grains having a metallic lustre:



This acid forms with the alkalis, salts which are easily soluble in water; with the earths and heavy metals, sparingly soluble salts. The *sodium salt*  $C^{20}H^{14}(C^6H^5)_3(C^6H^4SO^3Na)N^3$  is known as 'Nicholson's blue.' It is obtained perfectly pure by digesting the acid with a quantity of soda-ley not quite sufficient for saturation, filtering the solution, and evaporating. Dried at  $100^\circ$ , it forms a grey-black amorphous mass, which dissolves easily and with blue colour in hot water.—The *ammonium salt* obtained by dissolving the acid in ammonia, gives off a large quantity of ammonia when evaporated over the water-bath, and the residual colouring matter effloresces in rolled-up feathery masses, which move briskly about after drying, probably in consequence of a change of crystalline form.

The solutions of triphenylrosaniline-monosulphenates are but faintly coloured; the colour comes out with great intensity on acidulating the solution. If the solution is acidulated with acetic acid in the cold, the colouring matter remains unaltered; but it is precipitated by acetic acid from hot, and by mineral acids likewise from cold solutions. Wool dipped into the hot aqueous solution, especially if borax or water-glass be added, extracts the salts in the colourless state, and holds them so fast that they cannot be washed out by water; but, on dipping the wool thus prepared into an acid, the salt is decomposed and the colouring matter is set free, with its full lustre and great tinctorial power.

Under the influence of reducing agents, the triphenylrosaniline-sulphonates are easily converted into the corresponding leucaniline. Thus, on digesting the sodium-salt with excess of ammonium sulphide for two hours at  $100^\circ$ , and adding hydrochloric acid, leucaniline is separated as a white flocculent precipitate, easily soluble in acids and in alcohol, and reconverted by oxidising agents into the original compound.

2. *Triphenylrosaniline-disulphonic acid* is always obtained, together with the trisulphonic acid, when a solution of triphenylrosaniline hydrochloride is digested at  $60^\circ$  for five hours with a sixfold quantity of sulphuric acid. On pouring the solution into water the greater part of the colouring matter is precipitated in blue flocks consisting mainly of the disulphonic acid, whilst the trisulphonic acid remains dissolved, forming a liquid of fine blue colour.

The disulphonic acid is slightly soluble in water, insoluble in acid liquids. Its salts are more soluble than those of the monosulphonic acid, less soluble than those of the sulphonic acids of higher orders. Those of the alkali-metals are easily soluble in cold water. The sodium-salt is known commercially as 'soluble blue.' Those of the alkaline-earth-metals and heavy metals are mostly slightly soluble blue precipitates.

*Triphenylrosaniline-trisulphonic acid* is precipitated on adding hydrochloric acid or common salt to the blue liquid filtered from the disulphonic acid, in a mass of fine flocks. It is soluble in water and alcohol, and forms easily soluble salts with alkalis.

*Triphenylrosaniline-tetrasulphonic acid*, the highest sulpho-acid of the series, is obtained by digesting aniline blue in ten times its volume of fuming sulphuric acid at  $140^\circ$  for some hours. The product, poured into water, forms a deep blue solution, from which the excess of sulphuric acid may be removed by lead carbonate. The filtrate evaporated to dryness leaves the lead-salt of the tetrasulphonic acid, which, when purified by solution in a small quantity of water, precipitation with alcohol, and drying at  $100^\circ$ , has the composition  $C^{20}H^{14}(C^6H^5)_4(C^6H^4SO^3Pb)N^4$ .

The acid dissolves easily in water, forming a blue liquid, which dries up in the water-bath to a metallically lustrous amorphous mass: the salts which it forms with the alkalis are easily soluble in water, and dissolve with brown-red colour in excess of the alkali. Even the heavy metal salts are moderately soluble in water: the silver salt decomposes on boiling, with deposition of a silver speculum. Most of these tetrasulphonates are precipitated by alcohol from their aqueous solutions. Silk immersed in the alkaline or neutral solution removes the colouring matter with difficulty, from the acidulated solution with moderate facility.

The Sulpho-acids of the Aniline-violet (mono- and di-phenylrosaniline) are

obtained in a similar manner to those of aniline-blue, to which they are closely analogous in physical and chemical properties; but they are somewhat more difficult to prepare. A monosulphonic acid of *ethylphenylrosaniline* has also been obtained.

**Aniline Grey** is prepared by prolonged heating of 1 part of aniline with 5 parts liquid arsenic acid (? anhydride). The crude product is treated with a boiling mixture of 20 parts water and 5 parts hydrochloric acid, then filtered, and the undissolved portion is washed with water, then with dilute solution of sodium carbonate. The dry colouring matter is dissolved in alcohol mixed with  $\frac{1}{10}$ th part of sulphuric acid. Wool or silk may be coloured directly by very small quantities of it (Bloch, *Monsieur scientifique*, xi. 71).

**Aniline Lacquers.** F. Springmühl (*Dingl. polyt. J.* c.c. 224) prepares these lacquers by mixing alcoholic solutions of various resins with suitable aniline salts possessing the requisite tinctorial power. Bleached shellac, mixed in some cases with other resins, is dissolved in spirit containing 90-95 per cent. of real alcohol, by allowing the powdered resin to digest at a gentle heat in close vessels for about 24 hours before filtering through asbestos. Dilute solutions are concentrated on a water-bath. Sandarac added in small quantity increases the elasticity and durability of the lacquer, and oil of turpentine increases its lustre. Other resins are sometimes added, according as they suit the colours. A concentrated alcoholic solution of the colour is prepared separately, and added to the lacquer just before it is used. The objects to be covered with coloured lacquers should be bright and clear, and not too thick. Mica is treated in its settings, and, like glass, previously heated to about 30° C., to cause it to receive an uniform lacquer.

Aniline-violet is dissolved in the strongest alcohol; a few drops of acetic acid are added, and the whole gently heated with the alcoholic solution of the resin, so as not to produce any turbidity. The intensely coloured solution of the lacquer is then placed on the warm glass or mica, and is left to dry in a warm place (20° to 25° C.), till a clear and smooth, but intensely coloured coating has been formed on it, which is not affected by water or air.

Aniline-yellow, when transferred in like manner on transparent objects, lacks intensity. This can only be supplied by repeated coatings, generally, however, at the expense of uniformity.

Aniline-blue may be prepared in several ways. By boiling a shellac solution containing magenta with sodium carbonate, a blue lacquer is obtained, which is, however, little suitable for covering glass or mica, as the lacquer shrinks on drying, owing to the sodium carbonate retaining water. A shellac solution containing magenta, when gently heated on a glass plate, likewise turns blue, but the transparency is impaired by numerous small blisters; and it is best to use pure commercial aniline-blue dissolved in the lacquer, whenever it is desired to coat delicate articles, such as spectacles and other glasses, with a fine blue film.

Magenta produces with shellac a brilliant and perfectly transparent red, provided it has not to be exposed to a high temperature; the colour acquires considerable consistency by an admixture of gum-arabic. It is likewise recommended to employ alcoholic solutions of other resins, such as sandarac, Venice turpentine, &c.

Zinnilino, prepared from magenta by the action of nitrous acid, is employed in a similar manner for the production of yellow lacquers on account of its solubility in alcohol. It cannot, however, be heated above 100° C.

Aniline-green dissolved in alcohol, and added in moderate quantities to the lacquer, produces a bright lustrous and permanent covering; coralline, a lacquer acted upon by light. Emeraldine and ethylrosaniline-green should be dissolved just before being brought together with the concentrated lacquer.

Nearly all aniline colours may thus be employed for lacquers, provided they are pure enough, and do not contain too much water. They are for the most part better suited than extracts of dye-woods and other colouring matters, such as indigo, &c. Remarkably fine colours were obtained on glass and mica by employing solutions of gun-cotton in ether mixed with a little alcohol, and coloured by means of small quantities of aniline dyes. They leave on evaporation transparent layers, proportionate in thickness to the concentration of the solutions employed. The coating is rendered more elastic by the addition of a little oil of turpentine, and when put on cold glass plates can be detached readily and in a compact form. These coloured collodium skins may be cut into various shapes and figures, and fixed firmly by means of a little colourless gum to different transparent objects. Partially etched glass or mica may likewise be coated over with coloured lacquers, the etched portions becoming translucent, the others transparent. In case of failure, the lacquer can be easily removed by means of the respective solvents for the resins.

Mixtures of aniline colours and resins in alcoholic solution may be used for

colouring paper, leather, linen, &c.; but an easily soluble lake must be employed, and for equal bulks of alcohol used in dissolving, much less of the resin containing the lake must be taken. The colour may be applied to the paper as a pigment, or the paper may be soaked in the solution and hung up to dry (Springmühl, *ibid.* cii. 382).

**ANIMAL ORGANISM.** On the utilisation of certain inorganic constituents in the animal body, see NUTRITION.

**ANIMAL PROTEIDS.** See PROTEIDS.

**ANIMAL STARCH.** See STARCH.

**ANIMAL SUBSTANCES.** On the incineration of animal substances, see ASH.

On the question whether phosphoretted animal substances give off phosphoretted hydrogen during putrefaction, see PUTREFACTION.

**ANISHYDRA NILIDE**,  $C^6H^5NO = C^6H^5 \left\{ \begin{smallmatrix} OCH^3 \\ CH.N.C^6H^5 \end{smallmatrix} \right.$  isomeric with methyl-anhydronilide (see SALICYLID), is obtained by mixing anisic aldehyde with aniline. The mixture is clear at first, but soon becomes turbid, and separates into water and a lower layer, which when freed from excess of aniline, forms a yellow, scentless, tasteless, neutral oil, solidifying after several weeks to golden-yellow, fatty crystals of anishydranilide, easily soluble in alcohol, ether, and benzene (Schiff, *Ann. Ch. Pharm.* cl. 193).

**ANISIC ACID**,  $C^6H^5O^2$ .—*Methyl-amidanisic acid*,  $C^6H^5NO^2 = C^6H^5(NH.CH^3)O^2$ , isomeric with tyrosine, is formed by the action of methyl iodide on amidanisic acid. It crystallises in slender white needles, sparingly soluble in water, ether, and cold alcohol, but freely soluble in hot alcohol; melts above  $200^\circ$ . It unites with hydrochloric acid, forming the compound  $C^6H^5NO^2.HCl + H^2O$ , which crystallises in very small narrow plates, freely soluble in cold water and in hot hydrochloric acid, sparingly in cold hydrochloric acid. The silver salt is a white granular precipitate (Griess, *Deut. Chem. Ges. Ber.* v. 1042).

On the Action of Ammonia on Nitranisic Acid, see AMIDOBENZOIC ACID under BENZOIC ACID.

**ANISIC ALCOHOL**,  $C^6H^5O^2 = C^6H^5 \left\{ \begin{smallmatrix} OCH^3 \\ CH^2OH \end{smallmatrix} \right.$ .—The following directions for obtaining this alcohol in the pure state are given by Cannizzaro (*Gazzetta chimica italiana*, ii. 61). Anisic aldehyde—prepared by Rosso's method (1st Suppl. 172), and purified by combining it with acid sodium sulphite and decomposing the resulting compound with potassium carbonate, is mixed with three volumes of alcohol and four or five volumes of concentrated alcoholic solution of potash, and allowed to stand for some hours. When the mixture has become solid, water is added, and the alcohol removed by careful distillation in a current of steam. The residue, when cold, deposits an oily layer of impure anisic alcohol, the clear, supernatant liquid consisting of an aqueous solution of potassium hydrate and anisic alcohol, from which the latter may be removed by agitation with ether. The residue left on evaporating the ethereal solution yields anisic alcohol when submitted to fractional distillation, the portions which come over between  $250^\circ$  and  $260^\circ$  being collected apart. The first portions which come over should be tested with acid sodium sulphite, and if they give indication of the presence of anisic aldehyde, must be again submitted to the action of alcoholic potash. The alcohol, when purified by careful fractional distillation, melts at  $24^\circ$  to  $25^\circ$ ; by repeated distillation, however, it becomes oxidised and reconverted into anisic aldehyde. Long contact with alcoholic potash at an elevated temperature produces a change in this alcohol similar to that which benzylic alcohol undergoes, a methylated cresol being formed, whose boiling point is  $174^\circ$ .

*Methyl-salicylic alcohol*,  $C^6H^5O^2$ , isomeric with anisic alcohol, is prepared from saligenin,  $C^6H^5.CH^2OH.OH$ , by adding to it a molecule of potassium hydrate dissolved in methylic alcohol, and subsequently digesting the mixture with methylic iodide. When the action is terminated, an aqueous solution of potash is added and the methylic alcohol removed by distillation in a current of steam; the methylsalicylic alcohol can then be extracted from the residue by agitating it with ether. The impure alcohol left on the evaporation of the ethereal solution is submitted to fractional distillation, collecting apart the portion boiling at about  $240^\circ$ .

The boiling point of anisic alcohol at a pressure of 760 mm. reduced to  $0^\circ$ , is  $258.8^\circ$  (corrected), and that of methylsalicylic alcohol,  $247.5^\circ$  (corrected) under a pressure of 765.0 mm. Anisic alcohol when free from moisture melts at  $35^\circ$  and has a density of 1.10934 at  $25.85^\circ$ , and 1.06007 at  $49.75^\circ$ . Methylsalicylic alcohol maintains its transparency when surrounded by a bath of solid carbonic anhydride.

and ether, but gradually thickens and becomes semifluid: in one experiment it solidified. Its density is 1.389 at 0°, and 1.0532 at 100°.

The indices of refraction of these two isomeric alcohols have been determined by Blaserna (*ibid.* 60), for four lines of the spectrum, at the temperatures 28°, 29°, and 30°. The following table exhibits the values for the temperature 28°:—

	D	D	b	F
Anisic Alcohol:				
Sp. gr. 1.10934 at 25.85° .	1.53813	1.54308	1.55093	1.55594
" 1.10899 " 27.15° .	1.53802	1.54301	1.55080	1.55576
Methyl-salicylic Alcohol:				
Sp. gr. 1.12009 at 28° . .	1.53951	1.54440	1.55201	1.55703
" 1.12007 " 28° . .	1.54046	1.54534	1.55310	1.55796

Denoting the indices of refraction at a given temperature by  $n$ ,  $n'$ , and the densities by  $d$ ,  $d'$ , we may enquire whether the well-known formula of Laplace:

$$\frac{n^2 - 1}{d} = \frac{n'^2 - 1}{d'}$$

holds good with regard to these isomeric compounds.

The observations on the first portion of the anisic alcohol and the second portion of the methyl-salicylic alcohol, which are regarded as the best, give:

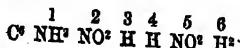
$$\begin{aligned} \text{for } t = 25.85^\circ, d = 1.10938; d' = 1.1176 \\ \text{and for } t = 28^\circ \quad n' = 1.54046 \text{ for the line C.} \end{aligned}$$

With these values the preceding equation gives  $n = 1.53717$ , whereas the observed value of  $n$  is 1.53813; the small difference between the observed and calculated values is most probably due to slight impurity in one or both of the alcohols.

**ANISIC ALDEHYDE**,  $C^6H^5O^2 = C^6H^4 \begin{smallmatrix} OCH^3 \\ CHO \end{smallmatrix}$ , is rapidly attacked at ordinary temperatures by phosphorus pentachloride, and on treating the product with water, the original aldehyde is reproduced (L. Henry, *Zeitschr. f. Chem.* [2] vi. 208). When 1 mol. anisic aldehyde and 2 mol. *acetamide* are heated together for some time to 120°–180°, and the yellow crystallised mass which forms on cooling is washed with water till it is nearly white, and then recrystallised from boiling water, the compound  $C^6H^4N^2O^2 (= C^6H^4O^2 + 2C^2H^3NO - H^2O)$  is obtained in nodular groups of shining needles, melting at 180°, insoluble in alcohol and ether, and precipitated from aqueous solution by alcohol.

*Benzamide* and anisaldehyde yield in like manner the compound  $C^6H^4N^2O^2$ , which however, must be recrystallised from alcohol, since it is insoluble in water and in ether. It likewise forms shining needle-shaped crystals melting at 192°. Both these compounds are decomposed by hydrochloric acid, with separation of anisic aldehyde, but they are not altered by potash, even at the boiling heat (A. Schuster, *Ann. Ch. Pharm.* cliv. 80).

**ANISOL**,  $C^6H^5O = C^6H^4(OCH^3)$ . *Action of Ammonia on the Nitro-anisols.*—Dinitranisol,  $C^6H^4(NO^2)_2.OCH^3$ , heated with strong aqueous ammonia in sealed tubes for three or four hours to 110°–120°, exchanges the group  $OCH^3$  for  $NH^2$ , and is converted into a dinitramidobenzene or dinitraniline,  $C^6H^4(NO^2)_2.NH^2$ , which is identical with the only dinitraniline hitherto known, inasmuch as both, when treated with nitrous acid, yield paranitrobenzene melting at 87°. This dinitraniline has, therefore, the constitution represented by the formula:



A similar structure must also belong to dinitranisol, dinitranisic acid, and their derivatives: dinitro-amidobenzoic (chrysanic acid), dinitroparaoxybenzoic acid, tramidobenzoic acid and triamidobenzene. Moreover, as the two lateral chains in anisic (methyl-paraoxybenzoic) acid undoubtedly also occupy the para-position, it



follows that the bodies above mentioned must be represented by the following formulæ:—

		1	2	3	4	5	6
Dinitranisol . . . . .	C <sup>6</sup>	OCH <sup>3</sup>	NO <sup>2</sup>	H	H	NO <sup>2</sup>	H
Dinitroanisic acid . . . .	C <sup>6</sup>	OCH <sup>3</sup>	NO <sup>2</sup>	H	CO <sup>2</sup> H	NO <sup>2</sup>	H
Chrysanisic acid . . . . .	C <sup>6</sup>	NH <sup>2</sup>	NO <sup>2</sup>	H	CO <sup>2</sup> H	NO <sup>2</sup>	H
Dinitroparaoxybenzoic acid	C <sup>6</sup>	OH	NO <sup>2</sup>	H	CO <sup>2</sup> H	NO <sup>2</sup>	H
Triamidobenzoic acid . . .	C <sup>6</sup>	NH <sup>2</sup>	NH <sup>2</sup>	H	CO <sup>2</sup> H	NH <sup>2</sup>	H
Triamidobenzene . . . . .	C <sup>6</sup>	NH <sup>2</sup>	NH <sup>2</sup>	H	H	NH <sup>2</sup>	H

The dinitranisol above mentioned is easily converted by the action of a mixture of nitric and sulphuric acids into trinitranisol, C<sup>6</sup>H<sup>3</sup>(NO<sup>2</sup>)<sup>3</sup>.OCH<sup>3</sup>, identical with that which is well known as methyl picrate, inasmuch as it is converted by potash into picric acid and by ammonia into picramide, which may also be formed by the action of ammonia on picryl chloride.

Now whichever of the three hydrogen-atoms in the dinitranisol may be replaced by the group NO<sup>2</sup>, it is clear that the three nitro-groups in the resulting trinitranisol must stand in relative positions which may be denoted by 1 : 2 : 4, and the same must be true respecting the three nitro-groups in picric acid (H. Salkowski, *Deut. Chem. Ges. Ber.* v. 872).

**ANISONITRIL**, C<sup>6</sup>H<sup>4</sup>NO = C<sup>6</sup>H<sup>4</sup> $\begin{Bmatrix} \text{OCH}^3 \\ \text{CN} \end{Bmatrix}$  (L. Henry, *Zeitschr. f. Chem.* [2]

vi. 209). Produced: 1. By dehydration of anisamide under the influence of heat. Anisamide melts at 137°–138°, and, when quickly heated in a small tubulated retort, distils gradually and almost without decomposition at about 295°, and sublimes in broad laminae; but, if heated for some time above its boiling point, it is partly converted into anisonitril, which distils over, more or less mixed with unaltered anisamide; the two bodies may be separated by ether, which easily dissolves the nitril. 2. By the action of pentasulphide, or pentachloride, of phosphorus on the amide. A mixture of anisamide with the pentachloride is distilled in a small tubulated retort passing into a condensing tube and provided with a thermometer. The reaction begins at ordinary temperatures; and on distilling the mixture, phosphorus oxychloride passes over first, the temperature then rising quickly to 250°–255°, where it remains constant, and a colourless liquid passes over, which solidifies in the condensing tube to a white crystalline mass.

Anisonitril separates from solution in ether in shining crystals, 1–2 centimeters long, and apparently consisting of oblique rectangular prisms. It has a pungent odour, dissolves very easily in ether, is soluble also in alcohol, carbon sulphide, and paraffin oils, insoluble in cold water, but moderately soluble in hot water, from which it separates on cooling in the form of small needles. It melts at 56°–57° to a colourless transparent liquid, which solidifies on cooling to a hard, brittle, crystalline mass; boils without decomposition under the ordinary atmospheric pressure at 253°–254°. Heated in a sealed tube to 120°–130° with a moderately concentrated solution of caustic potash, it is converted into anisic acid (melting at 175°). Fuming nitric acid acts on it very violently, converting it into nitro-anisonitril, C<sup>6</sup>H<sup>3</sup>(NO<sup>2</sup>) $\begin{Bmatrix} \text{OCH}^3 \\ \text{CN} \end{Bmatrix}$ , which crystallises from alcoholic solution in small nacreous needles, insoluble in water, soluble in alcohol, especially when hot, also in ether; melting at 149°–150°, and volatilising, when heated a little above its melting point, in thin transparent laminae.

**ANISURANIC ACID**, C<sup>6</sup>H<sup>3</sup>N<sup>2</sup>O<sup>4</sup>, is obtained on mixing the cold saturated solutions of potassium cyanate and hydrochloride of amidanisic acid, as a white amorphous precipitate; it is nearly insoluble in cold water, dissolves in about 2,000 parts of boiling water, and separates therefrom in delicate white needles. The calcium salt Ca(C<sup>6</sup>H<sup>3</sup>N<sup>2</sup>O<sup>4</sup>)<sup>2</sup> + 7H<sup>2</sup>O is precipitated in stellate groups of white needles on mixing the boiling ammoniacal solution of the acid with calcium chloride (Menschutkin, *Ann. Ch. Pharm.* cliii. 83).

**ANORTHITE.** See FELSPAR.

**ANTHRACENAMINE**, C<sup>14</sup>H<sup>11</sup>N = C<sup>14</sup>H<sup>9</sup>(NH<sup>2</sup>) (Phipson, *Chemical News*, xxvii. 97). A base obtained by treating mononitroanthracene with tin and hydrochloric acid. The immediate product of the reaction is a compound of anthracenamine hydrochloride with tin chloride, from which the base may be separated by potash, which dissolves out the tin; the operation must, however, be repeated to get rid of the tin completely.

Anthracenamine is a pale yellow powder, forming soluble and crystallisable salts with sulphuric and hydrochloric acids. It is very soluble in alcohol, but slightly

2nd Sup.

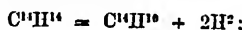
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soluble in water; its odour is very slight, and its taste hot, pungent, and persistent, very like that of the unknown substance which exists in the *Arum maculatum*. It is easily decomposed. Its acid salts produce with potassium dichromate a characteristic emerald-green colour, and finally precipitate a powder of this colour which is soluble in alcohol. This solution presents no marked peculiarity when viewed in the spectro-scope. The reaction is as characteristic of anthracenamine as the blue colour produced in similar circumstances is of naphthylamine. It is not obtained, however, with lead peroxide or with calcium hypochlorite, but it is obtained with concentrated nitric acid.

**ANTHRACENE,  $C^{14}H^{10}$ .** *Formation*.—1. The formation of anthracene from dibenzyl (1st Suppl. 176), is accompanied by that of a hydrocarbon,  $C^{14}H^{14}$ , boiling at about  $280^{\circ}$ , which has hitherto been regarded as dibenzyl,  $C^6H^5\{CH^2[CH^2(C^6H^5)]\}$ . Van Dorp, however, has shown (*Deut. Chem. Ges. Ber.* v. 1070), that when oxidised by potassium dichromate and sulphuric acid, it yields benzoyl-benzoic acid,  $C^6H^5(C^6H^5O).CO^2H$ ; hence it must consist of benzyl-toluene,  $C^6H^5.CH^2[C^6H^4(CH^3)]$ :

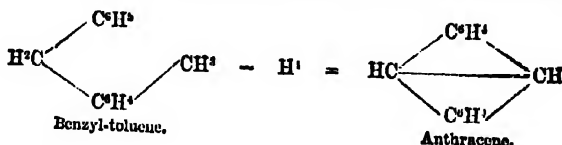


Now, when this hydrocarbon, obtained as above, is passed over red-hot pumice, it is resolved into free hydrogen and anthracene:



and the same result is obtained when benzyl-toluene, prepared by Zincke's method, viz., by heating a mixture of benzyl chloride and toluene with zinc-dust (see BENZYL-TOLUENE), is treated in a similar manner. The anthracene condensed in the receiver is saturated with unaltered benzyl-toluene, which may be separated by draining and pressure, and when subjected to the same treatment, yields a further quantity of anthracene. The anthracene thus obtained is quite pure, and agrees in every respect with anthracene from coal-tar. The quantity obtained in the first operation is about 10 p. c. of the benzyl-toluene.

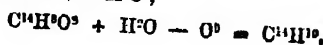
The constitutional formula of benzyl-toluene, obtained by Zincke's process, has not been exactly determined; but whichever of the possible isomerides of the formula,  $C^6H^5.CH^2.C^6H^4.CH^3$ , may be supposed to represent its constitution, it is impossible to explain the formation of anthracene from it by elimination of hydrogen, if anthracene be supposed to have the constitution originally suggested by Gräbe and Liebermann (1st Suppl. 214). If, however, anthracene be represented by the second constitutional formula proposed by those chemists (*Ann. Ch. Pharm. Suppl.* vii. 251), its synthesis from benzyl-toluene is easily explained, supposing the latter to be an ortho-derivative (1 : 2) of benzene. The following formulae may represent the transformation:



Berthelot, by passing toluene vapour through a red-hot tube, obtained—besides other products—anthracene and a liquid hydrocarbon,  $C^{14}H^{14}$ , boiling at  $179^{\circ}$ ; this was doubtless benzyl-toluene, and the anthracene was produced by its decomposition as above.

2. Anthracene is formed by reduction of oxidised organic compounds containing the same number of carbon-atoms: a. From anthroquinone, by the action of zinc-dust in presence of hydrochloric acid or of strong potash- or soda-ley at the boiling heat (Böttger, *J. pr. Chem.* [2] ii. 133).

b. From rufgalliac acid,  $C^{14}H^8O^8$ ,



Now, rufgallie acid contains the elements of 2 mol. gallie (dioxysalicylic) acid, minus 2 mol. water:  $2C^7H^6O^3 - 2H^2O = C^{14}H^{10}O^3$ , and is formed by heating gallie acid with sulphuric acid. The reaction above mentioned affords, therefore, the means of passing, by a definite transformation at a moderate heat, from the benzene series to the anthracene series (Jaffé, *Deut. Chem. Ges. Ber.* iii. 694).

γ. Anthracene is also said to be formed by the action of zinc-dust on curcumin (Kachler, *ibid.* 713).

**Preparation and Purification.**—For the preparation of anthracene from coal-tar, J. Gessert introduces the last pasty portions (green grease) of the coal-tar distillation (which should not be carried beyond the point at which white pitch is produced), first into a centrifugal machine, and then into a hydraulic press at  $40^\circ$ , or subjects the mass heated to  $30^\circ$ – $40^\circ$  directly to pressure in a filter-press. The pressed mass contains about 60 p. c. of anthracene; for further purification it is boiled out with light tar-oil or petroleum-naphtha, and finally heated till it melts. The residue contains 95 p. c. anthracene (*Dingl. polyt. J. exvi.* 543).

For the purification of crude anthracene contaminated with oily matters, Schuller (*ibid.* 546) recommends the following process:—The crude anthracene is carefully heated to commencing ebullition in a capacious retort connected with a tubulated receiver of glass or earthenware, the lower aperture of which is closed with a fine wire sieve. A strong current of air is then blown into the retort with a pair of bellows, whereby the anthracene is driven over in a very short time nearly pure and dry, and condenses in the receiver as a faintly yellowish snowy mass. By this method a quantity of anthracene, the purification of which by recrystallisation or sublimation would take several days, may be purified in as many hours; moreover, it is obtained in a pulverulent form, in which it is very readily acted on by oxidising agents. Anthraquinone, prepared from crude anthracene, may also be obtained by this method in the form of a light yellow powder resembling flowers of sulphur.

Fritzsche, by exposing a solution of anthracene in coal-tar naphtha to sunshine till it became colourless, obtained the anthracene in crystals exhibiting a beautiful violet-blue fluorescence (*1st Suppl.* 177). The same fluorescent crystals are obtained, according to v. Wartha (*Zeitschr. f. Chem.* [2] vi. 695), by melting anthracene with sulphur. Streams of hydrogen sulphide are then given off, and part of the anthracene which is in excess, sublimes in fine crystals exhibiting the violet-blue fluorescence, whereas the same anthracene, if repeatedly recrystallised without treatment with sulphur, and then sublimed in a vacuum, yields snow-white, non-fluorescent crystals.

The sublimation of anthracene is best effected according to v. Wartha (*ibid.* 545) in a vacuum, the apparatus consisting of a wide tube connected with a mercury- or water-pump.

For the valuation of commercial anthracene, 5 or 10 grams of the substance may be pressed between paper and warm plates, then boiled with at least an equal weight of alcohol, separated by filtration after cooling, then washed with alcohol, dried, and weighed (Gessert).

On the preparation of Anthracene from coal-tar and of Dyo-stuffs from anthracene, see Brönnner u. Gutzkow (*Dingl. polyt. J.* cxi. 545; *Chem. Soc. J.* [2] ix. 1222).

**Action of Carbonyl Chloride (phosgene) on Anthracene.**—Graebe u. Liebermann, by heating anthracene with liquid carbonyl chloride in sealed tubes, obtained a yellow crystalline chlorinated compound, which when heated with aqueous sodium carbonate was converted into anthracene-carbonic acid,  $C^{14}H^8.CO^2H$  (*1st Suppl.* 179). Berthelot, on the other hand (*Bull. Soc. Chim.* [2] xiii. 391), obtained, by the same process, nothing but a mixture of hydrocarbons having a percentage composition agreeing with the formula  $C^{14}H^8$ : whence it would appear that the action of phosgene at high temperatures on anthracene consists merely in the abstraction of hydrogen. But the results obtained by Graebe and Liebermann, according to which the reaction takes place in the manner represented by the equation,  $C^{14}H^{10} + COCl^2 = HCl + C^{14}H^8.COCl$ , appear too definite to be doubted.

**Action of Chromic Oxychloride.** This acid chloride converts anthracene into anthraquinone together with a small quantity of dichloranthraquinone (Carstanjen, *Zeitschr. f. Chem.* [2] vi. 206).

**Nitroanthracenes.**—When nitric acid and anthracene in equal numbers of molecules are heated in alcoholic solution, the liquid assumes a red colour, and after some time red crystals of mononitro-anthracene,  $C^{14}H^9NO^2$ , separate out (about 80 p. c. of the anthracene). This compound is insoluble in cold alcohol and benzene; from a hot alcoholic solution it crystallises in needles grouped in stars. When heated it sublimes in needles, which have the greatest resemblance to sublimed alizarin. The formation of this compound in alcoholic solution is the more interest-

ing, as the pure nitro-compounds are not formed by the action of nitric acid on solid anthracene.

Besides the mononitro-compound, dinitro-anthracene is also formed, the quantity of it increasing if more nitric acid is employed. It is moderately soluble in hot alcohol and benzene, and sublimes in colourless plates (Bolley, *Zeitschr. f. Chem.*, [2] vii. 45).

When mononitro-anthracene is heated with zinc and a solution of caustic potash, the solution acquires first a red and afterwards a yellow colour. On exhausting it with hot alcohol and mixing this solution with water and hydrochloric acid, a body is precipitated, which is soluble in alcohol and benzene, and when heated sublimes in colourless plates.

DIMETHYL-ANTHRACENE,  $C^{10}H^{14} = C^{11}H^8(CH^3)^2$ , is formed, together with an oily body (probably *xylyl-xylene*,  $C^{10}H^{18}$ ), by exposing *xylyl chloride*,  $C^8H^4.CH^3.(CH^2Cl)$  (prepared by the action of chlorine on boiling coal-tar xylene), to the action of water at  $200^\circ$  in sealed tubes:



the reaction being analogous to that by which anthracene and benzyl-toluene are formed from benzyl chloride (p. 82).

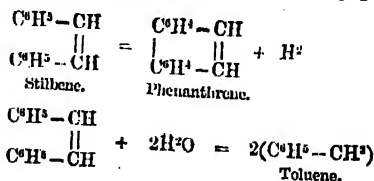
The product is a brown aromatic oil, which when distilled, gives off *xylyl-xylene*, as a pale yellow oil at about the boiling point of mercury, and towards the end of the distillation, dimethyl-anthracene, which crystallises in the neck of the retort. The *xylyl-xylene* passed through a red-hot tube is almost wholly resolved into dimethyl-anthracene and free hydrogen.

Dimethyl-anthracene closely resembles anthracene; it crystallises in large glistening plates, which are white and fluorescent when perfectly pure, and melt at about  $200^\circ$ . By oxidation with chromic acid it yields a product which may be sublimed in yellow plates melting at  $153^\circ$ ; probably dimethyl-anthraquinone. A small quantity of a second body of higher melting point is also formed (A. van Dorp, *Deut. Chem. Ges. Ber.* v. 674.).

**ANTHRACENE, ISOMERIDES OF.**—I. PHENANTHRENE (Graebe, *Deut. Chem. Ges. Ber.* v. 861; *Ann. Ch. Pharm.* clxvii. 131. Fittig a. Ostermayer, *Deut. Chem. Ges. Ber.* v. 933; *Ann. Ch. Pharm.* clxvi. 361).—*Occurrence.* This hydrocarbon, differing from anthracene in its melting point and in several of its reactions, has been obtained from crude anthracene, and from the liquid portion of coal-tar oil which boils above  $300^\circ$ :—1. In the purification of crude anthracene on the large scale, Glaser obtained a dark yellowish brown crystalline mass, melting at a few degrees below  $100^\circ$ , and boiling between  $310^\circ$  and  $360^\circ$ . From this product phenanthrene may be isolated by distillation and repeated crystallisation from alcohol. It is better, however, first to prepare the *picric acid* compound, by dissolving 1 part of the crude material and  $1\frac{1}{2}$  part of *picric acid* in hot coal-tar naphtha boiling between  $100^\circ$  and  $140^\circ$ ; the solution on cooling deposits the *picrate*  $C^{14}H^{10}.C^8H^4(NO_2^3)O^3H$  in long golden-yellow needles or prisms melting at  $145^\circ$ . This compound is resolved, slowly by water, and quickly by alkalis, into *picric acid* and phenanthrene (Graebe).

2. Fittig a. Ostermayer obtained phenanthrene from a neutral coal-tar oil boiling between  $300^\circ$  and  $400^\circ$ , by subjecting this oil to fractional distillation, and cooling the portions which boiled above  $300^\circ$ , to  $0^\circ$ . The crystals thereby separated were dried in bibulous paper and repeatedly crystallised from alcohol to remove anthracene and other bodies.

*Formation.* Phenanthrene is formed, together with toluene, by passing *stilbene* through a red-hot tube:



It is also formed by the same reaction from dibenzyl, which, as Dreher a. Otto have shown, is first resolved into toluene and stilbene:  $2C^{14}H^{14} = 2C^8H^8 + C^{10}H^{12}$ .

These reactions render it probable that phenanthrene has the constitution originally assigned by Graebe a. Liebermann to anthracene, that is to say, that it is diphenyl  $C^8H^8-C^8H^8$ , in which two atoms of hydrogen are replaced by the group  $-CH=CH-$  (Graebe).

Phenanthrene crystallises in small plates, which generally have a yellowish colour, but when quite pure, are brilliant and colourless, and exhibit a blue fluorescence, fainter, however, than that of anthracene. It is sparingly soluble in cold alcohol, but dissolves readily in hot alcohol, ether, benzene, acetic acid, and carbon sulphide. It melts at  $99^{\circ}$ – $100^{\circ}$ , and sublimes very readily, but boils only at a temperature much above  $300^{\circ}$  (Fittig & Ostermayer); melts at  $100^{\circ}$  and boils at  $340^{\circ}$ , with the whole column of mercury in the vapour (Graebe).

**Oxidation.** Phenanthrene gently heated with potassium dichromate and dilute sulphuric acid is oxidised to phenanthrenequinone,  $C^{14}H^{10}O^2$  (Fittig & Ostermayer). The same compound is formed by gradually adding a solution of chromic acid in acetic acid to a solution of phenanthrene in hot glacial acetic acid (Graebe). This reaction affords the means of detecting the presence of phenanthrene in crude anthracene. On heating that substance with acetic acid and chromic acid, treating the product with sodium carbonate to remove acids, and heating the undissolved portion with a solution of *acid sodium sulphite*, the phenanthrenequinone is alone dissolved, and may be precipitated from the solution by acids, and recognised by its properties (see ANTHRAQUINONE, p. 93).

**Reduction.** Phenanthrene is not reduced by sodium-amalgam in alcoholic solution; but by heating it with hydriodic acid and phosphorus to  $200^{\circ}$ , it is converted into tetrahydrophenanthrene,  $C^{14}H^{14}$ , a liquid boiling at  $300^{\circ}$ – $310^{\circ}$ , whilst at  $240^{\circ}$  the hydrocarbon  $C^{14}H^{12}$  is formed, which is also liquid, and boils below  $300^{\circ}$  (Graebe).

**Phenanthrene Dibromide**,  $C^{14}H^{10}Br^2$ , is formed on adding bromine drop by drop to an ethereal solution of phenanthrene, and crystallises in four-sided prisms: it is very unstable, decomposing spontaneously on keeping (F. and O.).

**Phenanthrene Picric Acid**,  $C^{14}H^9 \cdot C^6H^3(NO^2)_3O$ , is obtained in the manner already mentioned (p. 84), in long, golden yellow or reddish-yellow prisms; from a mixture of the cold alcoholic solutions of phenanthrene and picric acid it separates in red needles. It melts at  $145^{\circ}$  (Graebe), at  $143^{\circ}$  (F. and O.). It may be boiled with a large quantity of alcohol without decomposition, but water resolves it into phenanthrene and picric acid.

**Nitrophenanthrenes.** Cold concentrated nitric acid converts phenanthrene into the mononitro-compound  $C^{14}H^9(NO^2)$ , which, by solution in acetic acid and addition of water, is obtained as a yellow crystalline precipitate melting between  $70^{\circ}$  and  $80^{\circ}$ . If the nitric acid is not kept cold, dinitrophenanthrene,  $C^{14}H^8(NO^2)^2$ , is formed, and may be obtained in quantity by heating to  $100^{\circ}$ ; it separates from acetic acid in yellow crystals melting between  $150^{\circ}$ – $160^{\circ}$  (Graebe).

**Phenanthrene-sulphonic acid**,  $C^{14}H^9SO^3H$ , is produced, together with a small quantity of the disulphonic acid, by heating phenanthrene with sulphuric acid to  $100^{\circ}$ . Separated from the lead salt by hydrogen sulphide, it forms a crystalline mass, more freely soluble in hot than in cold water. The *calcium salt*  $Ca(C^{14}H^8SO^3)^2 + 4H^2O$  crystallises in small plates, and dissolves readily in alcohol and in hot water. The *lead salt*  $Pb(C^{14}H^8SO^3)^2 + 2H^2O$  is freely soluble in water and in alcohol, and does not crystallise well. The *barium salt* has similar properties (Graebe).

II. Another isomeride of anthracene, distinguished by its much higher melting point, is said by Ernst Schmidt (*Deut. Chem. Ges. Ber.* v. 930) to be formed by the reduction of a red modification of mononitro-anthracene. When anthracene is nitrated by Bolley's method in alcoholic solution, a mixture of isomeric mononitro-derivatives is obtained, consisting of a red and a white mononitro-anthracene. If the former be acted upon by tin and hydrochloric acid, the red body disappears after a time, and is replaced by a yellowish-grey substance, readily purified by recrystallisation from alcohol or benzene. The same compound is formed in small quantity on subliming red mononitro-anthracene, together with a yellow substance (possibly dinitro-anthracene), of lower melting point.

This body has the composition  $C^{14}H^{10}$ ; it crystallises in thin, silky, glistening plates, which exhibit a violet-blue fluorescence; melts at  $247^{\circ}$ . It is almost insoluble in cold, but more soluble in hot alcohol; benzene, chloroform, and carbon sulphide dissolve it readily. It unites with picric acid, forming a compound which crystallises in reddish-yellow needles. It is not affected, even by prolonged heating, with nitric acid of sp. gr. 1.2, but is readily acted upon by more concentrated or fuming acid. Sulphuric acid does not act upon it at  $100^{\circ}$ , but on further heating dissolves it, and converts it into a sulpho-acid, forming a bluish-green solution, without the least carbonisation.

The action of tin and hydrochloric acid on mononitro-anthracene likewise gives rise to *amidanthracene* or *anthracenamine* (p. 81), (Schmidt).

**ANTHRACENE-ORANGE** (Böttger, *J. pr. Chem.* [2] ii. 130; *Chem. Centrbl.* 1870, 559).—A derivative of nitro-anthracene obtained by the action of reducing agents on nitro-anthraquinone. Anthraquinone is heated to about  $140^{\circ}$  with about 16 parts by weight of a mixture of equal volumes of sulphuric acid (sp. gr. 1.84) and nitric acid (sp. gr. 1.5), and the resulting solution is immediately poured into cold water. The nitro-compound which separates is washed and treated with a solution of potassium or sodium stannite (prepared by adding a fresh solution of stannous chloride to potash- or soda-ley, till the liquid begins to show turbidity, and filtering after clarification), whereby an emerald-green liquid is produced, which, when heated to the boiling point, soon deposits anthracene-orange as a flocculent powder of a nearly vermilion-red colour.

Anthracene-orange melts at  $225^{\circ}$ , and sublimes at a higher temperature in splendid garnet-red feathery needles, having a greenish surface-lustre. It dissolves in ether, acetic ether, acetone, aldehyde, alcohol, and wood-spirit, also in benzene and amyl-alcohol, only slightly in carbon sulphide, not at all in light petroleum oil. Sulphuric acid dissolves it without decomposition, even at the boiling heat, and the solution is precipitated by water. Nitric acid of sp. gr. 1.2 likewise exerts at ordinary temperatures only a solvent action. Potash and soda have no action on this compound; mercuric nitrate converts it, on heating, into a deep violet powder, which dissolves with the same colour in alcohol or ether.

The above mentioned emerald-green solution, if mixed, without warming, with an excess of dilute sulphuric acid, deposits a brownish-red precipitate, which, when dried and dissolved in alcohol, yields, after the alcohol has been distilled off, a brown colouring matter, soluble, with deep purple-red colour, in acetic ether and in alcohol.

**ANTHRACHRYSONE**,  $C^{14}H^{10}O^2$  (Barth n. Senhofer, *Ann. Ch. Pharm.* clxiv. 109).—A compound produced by the dry distillation of dioxybenzoic acid, or by heating that compound for an hour with four or five times its weight of strong sulphuric acid:



On adding water to the dark blood-red solution obtained by the latter process, the anthrachryson separates as a dark green powder, which may be purified by dissolving it in alcohol and boiling the solution with animal charcoal. From the yellow filtrate it is precipitated by water in crystalline flocks, having the composition  $C^{14}H^{10}O^4 + 2H^2O$ , and becoming anhydrous when dried at  $100^{\circ}$ .

This body is not an anhydride of dioxybenzoic acid, as by heating it with water or potash it is, according to the temperature, either not altered at all or completely destroyed. By heating it with zinc-dust it is reduced to anthracene; it is, therefore, a *tetraoxyanthraquinone*, and its formation is analogous to that of rufigallic acid from gallic acid, or of rufiopin from opianic acid.

Anthrachryson forms a golden-yellow crystalline powder, which, when heated, gives off a quinone-like smell, but does not melt even at  $320^{\circ}$ . It can be distilled without decomposition, and is but sparingly soluble in alcohol, and less so in benzene and toluene. Water dissolves only traces of it; in dilute sulphuric acid or hydrochloric acid or carbon sulphide it is quite insoluble. The best solvent for it is glacial acetic acid; water precipitates it from this solution in greenish-yellow flakes. Although possessing the characteristic properties of a quinone, anthrachryson is not acted upon by sodium-amalgam.

On heating it with a large quantity of water and freshly-precipitated barium carbonate, the compound  $(C^{14}H^{10}O^4)_2Ba + 11H^2O$  separates on standing in dark red crystalline flakes. The same salt is obtained in needles half an inch long when anthrachryson is heated with the right quantity of baryta-water and the solution is concentrated. On adding barium chloride to a solution of the ammonium salt, dark red needles, having the composition  $C^{14}H^{10}O^4Ba$ , gradually crystallise out. When calcium chloride is added to the ammoniacal solution, the calcium salt is obtained as a precipitate consisting of light red microscopic needles. The magnesium and aluminium salts are amorphous red precipitates; the copper- and silver-salts, brown amorphous masses. By fusing anthrachryson with potash, a large quantity of a humus-like substance is formed, together with a small quantity of a crystalline body. Anthrachryson dyes on iron-mordants a brown colour, and on alumina-mordants it produces a colour like that of alizarin, but duller.

**ANTHRAFLAVIC ACID**,  $C^{14}H^{10}O^4$  (Schunck, *Proc. Lit. Phil. Soc. of Manchester*, x. 133. Liebermann, *Deut. Chem. Ges. Ber.* iv. 103. Perkin, *Chem. Soc. J.* [2] ix. 1109; xi. 19).—An acid, isomeric with alizarin, obtained as a bye-product in the preparation of the latter by melting disulphanthraquinonic acid with potash (1st Suppl. 84), especially when the action is weakened by admixture of chalk.

To prepare it, commercial artificial alizarin is boiled with baryta-water, and the orange-coloured filtered solution of barium anthraflavate is precipitated with hydrochloric acid; or the crude alizarin is dissolved in boiling dilute soda-ley; milk of lime is added till the solution, still kept boiling, becomes yellow or orange; this liquid is filtered from the purple calcium salt; and the anthraflavic acid is precipitated by hydrochloric acid, washed on a filter, and dried. It is then powdered and boiled with alcohol; the dark coloured liquid, when cold, is filtered off; the undissolved portion is treated with weak caustic soda; and the resulting solution is filtered to remove insoluble impurities,\* then boiled, mixed with excess of barium chloride, and rapidly filtered. On cooling, the barium anthraflavate is deposited in needles, which may be purified by three or four crystallisations from water (Perkin).

Schunck assigned to anthraflavic acid the formula  $C^{12}H^{10}O^4$ . Liebermann regards it as monoxanthraquinone,  $C^{12}H^{10}O^4$ , identical with that produced by the action of potash on monobromanthraquinone or anthraquinone-monosulphonic acid (p. 92). But from Perkin's analysis of the product obtained from commercial alizarin, and of its derivatives, it appears to be isomeric with alizarin, that is to say, to have the composition of dioxanthraquinone. Perkin, moreover, points out that both these oxanthraquinones are probably formed in the manufacture of alizarin, and are separated in the treatment with baryta-water above described, anthraflavic acid being nearly insoluble in cold baryta-water, and separating out as a barium-salt, whereas monoxanthraquinone, which, according to Liebermann, is easily soluble in cold baryta-water, remains in the mother-liquor.

Anthraflavic acid separated from the pure barium-salt by hydrochloric acid, and purified by washing, drying, and crystallisation from boiling alcohol, forms beautiful bright yellow silky needles, generally arranged in radiate groups. After drying in a vacuum, it is perfectly anhydrous, and does not lose weight even when heated to  $180^\circ$  (Perkin).

It is chiefly the presence of anthraflavic acid in crude alizarin that affects the colour of the alkaline solution, changing the violet due to alizarin into purple, or when present in larger quantity, into red. For the same reason an alkaline solution of crude alizarin does not show the absorption-bands in the spectrum so distinctly as one of pure alizarin. Alkaline, as well as alcoholic solutions of anthraflavic acid, absorb the blue end of the spectrum very powerfully, though no bands are visible, even with very dilute solutions. A solution of the acid in concentrated sulphuric acid, if not too dark, shows, however, a broad but well defined absorption-band at the extreme edge of the blue, bordering on the green, accompanied by a total absorption of the violet, as seen with the other solutions (Schunck).

When pure anthraflavic acid is dissolved in excess of caustic potash, and the solution is boiled down to dryness, a yellow residue is left, which, after being carefully heated almost to fusion, dissolves in water with a red colour; this solution contains alizarin.

Anthraflavic acid, like alizarin, appears to be reduced to anthracene by zinc-powder (Schunck).

Anthraflavic acid is bibasic. It is but a weak acid, though it forms well defined salts, some of which are regularly crystallised. All its soluble salts give yellow solutions, but it has no dyeing properties.

Barium anthraflavate crystallises in reddish-brown hydrated needles, which, when dried at  $150^\circ$ , have the composition,  $2C^{12}H^8BaO^4 \cdot H^2O$ , and do not undergo any further diminution in weight even when heated to  $180^\circ$ . When dried in a vacuum or at  $100^\circ$ , it contains a larger quantity of water, corresponding with the formula  $2C^{12}H^8BaO^4 \cdot 3H^2O$ . When freshly prepared, it contains a much larger quantity. An air-dried specimen heated to  $100^\circ$  lost 18.2 p. c., answering to the formula  $2C^{12}H^8BaO^4 \cdot 3H^2O + 10aq.$ , which requires 18.3 p. c. for 10aq. (Perkin).

*Diacetyl-anthraflavic acid*,  $C^{12}H^{10}O^6 = C^{12}H^8O^2 \cdot \begin{Bmatrix} C^2H^3O \\ OC^2H^3O \end{Bmatrix}$ . — Anthraflavic acid, heated to about  $160^\circ$  in sealed tubes with acetic anhydride, gradually dissolves, and if the temperature be kept up for four or five hours, entirely disappears, the liquid on cooling depositing diacetyl-anthraflavic acid, which may be purified by one or two recrystallisations from glacial acetic acid. It then forms small, beautiful crystals of a very yellow colour, and somewhat like benzoic acid in shape. It melts at  $228^\circ - 229^\circ$ , and may be volatilised without decomposition. It dissolves sparingly in alcohol; with moderate facility in glacial acetic acid. Strong sulphuric acid dissolves it, forming an orange-red liquid, from which water throws down a yellow precipitate, apparently consisting of anthraflavic acid. Alcoholic potash decomposes it, reproducing anthraflavic acid.

\* These impurities are present in considerable quantities, and when heated, give a sublimate of pale yellow needles, like anthraquinone, leaving a carbonaceous residue.

*Dibenzoyl-anthraflavic acid*,  $C^{28}H^{16}O^6 = C^{14}H^8O^2 \left\{ \begin{smallmatrix} OC^7H^3O \\ OC^7H^3O \end{smallmatrix} \right.$ , is formed by boiling anthraflavic acid with excess of benzoyl chloride, and separates from the liquid, on cooling, in needle-shaped crystals, which may be purified by repeated washing with glacial acetic acid, and then with alcohol. It is of a pale yellow colour, melts at  $275^\circ$ ; is insoluble, or nearly so, in alcohol, very slightly soluble in boiling glacial acetic acid, from which it is deposited in fine needles on cooling. Alcoholic potash acts upon it but slowly. With strong sulphuric it reacts like acetyl-anthraflavic acid, but dissolves less readily (Perkin).

**ANTHRAHYDROQUINONE**,  $C^{14}H^8O^2 = C^{14}H^8(OH)^2$ . When a dilute solution of caustic soda is added to a mixture of anthraquinone and zinc-dust, the liquid assumes a red colour, and the anthraquinone gradually dissolves. On adding an acid to this solution, the product of reduction is obtained as a yellow precipitate, which when exposed to the air is soon reconverted into anthraquinone. To obtain the pure product it must be precipitated, washed, and dried in an atmosphere of carbon dioxide. The analysis of the compound gave numbers corresponding with the formula  $C^{14}H^8(OH)^2$ , but it probably contained also some anthraquinhydrone  $\begin{smallmatrix} C^{14}H^8OH \\ C^{14}H^8OH \end{smallmatrix} (O^2)^2$  (Graebe u. Liebermann, *Deut. Chem. Ges. Ber.* v. 15). Anthrahydroquinone is likewise produced by prolonged fusion of anthraquinone with potassium hydrate at temperatures above  $250^\circ$  (*ibid.* iii. 634).

**ANTHRAPURPURIN**,  $C^{14}H^8O^2$  (Perkin, *Chem. Soc. J.* [2] x. 659; xi. 425). A colouring matter, isomeric with the purpurin of madder, obtained as a secondary product in the preparation of alizarin from anthracene. It may be separated from alizarin by precipitating the two colouring matters together with alumina, and treating the resulting lake with an alkaline carbonate, the anthrapurpurin being then dissolved out, while the alizarin lake remains unattacked. The process, however, is slow, involving tedious filtrations, and it is better to dissolve the crude colouring matter in dilute sodium carbonate, and agitate the resulting solution with freshly precipitated alumina, which combines with the alizarin, leaving the anthrapurpurin in solution. This is filtered off from the alizarin lake, heated to boiling, and acidified with hydrochloric acid. The colouring matter which is precipitated is then collected on a filter, washed, and dried.

The anthrapurpurin thus obtained is very impure, being associated with a substance which dyes alumina-mordant of an orange colour, as well as with anthraflavic acid, &c. These impurities can be removed to a considerable extent by repeatedly boiling the product with alcohol, anthrapurpurin being but little soluble in that liquid. For further purification, it is best to digest the product with boiling alcoholic soda, collect the difficultly soluble sodium-compound which forms, on a filter, and wash it several times with dilute alcoholic soda. It is then dissolved in water and boiled, and the colouring matter is precipitated with barium chloride. The purple barium-compound thus obtained is collected on a filter, washed a few times with hot water, and then decomposed by boiling with sodium carbonate; the resulting purple solution is filtered off, and the anthrapurpurin precipitated with hydrochloric acid. After this precipitate has been collected on a filter, it is well washed with water, dried, and finally twice crystallised from glacial acetic acid.

Anthrapurpurin thus purified gave in several analyses from 65.11 to 66.12 p. c. carbon, and 3.17 to 3.47 hydrogen: the formula  $C^{14}H^8O^2$  requires 65.62 carbon and 3.12 hydrogen. This formula is confirmed by the analyses of the acetyl and benzoyl derivatives.

Anthrapurpurin when heated, first fuses and then evolves orange-coloured vapours, which condense as yellowish-red leaves or needles, but by far the largest quantity of the substance is carbonised. It is difficultly soluble in alcohol and ether, but rather more soluble in glacial acetic acid. It is deposited from the boiling acetic solution on standing in small fungoid-looking groups of minute orange-coloured needles. These groups are generally not more than 2 or 3 m.m. in diameter, and from the direction of the crystals, generally appear lighter on the under side than on the upper. They can only be seen to advantage under the microscope. As this substance dissolves but slowly in boiling glacial acetic acid, it is sometimes necessary to distil off part of the acid before the resulting solution can be made to deposit crystals.

Anthrapurpurin is very slightly soluble in water, and may be removed from its aqueous solution by means of ether. When heated with powdered zinc, it yields small quantities of a hydrocarbon, which, when purified, has the melting point and other properties of ordinary anthracene.

The solution of anthrapurpurin in caustic potash gives two absorption-bands situated in the same region of the spectrum as those produced by alkaline solutions of



alizarin; they are also produced by alkaline solutions of triacetyl-alizarin. In solutions prepared with caustic alkalis, these absorption-bands are more decided than in those in which alkaline carbonates are used; in either case, however, they are much fainter than those of alizarin. The ammoniacal solution does not appear to give bands, nor does the ethereal solution of the colouring matter; in the latter case, however, the violet is almost entirely absorbed.

As a dyeing agent, anthrapurpurin has about the same affinity for mordants as alizarin. The colours it produces are also analogous to some extent, as it produces red with alumina, purple and black with iron mordants. There is, however, a considerable difference in the shade of colour produced, the reds being much purer and less blue than those of alizarin, whilst the purples are bluer and the blacks more intense. In fastness against soap and light the colours are quite equal to those produced with alizarin.

When used to dye Turkey-red, anthrapurpurin produces very brilliant colours of a scarlet shade, which are of remarkable permanence.

Ordinary *nitric acid* acts rapidly on anthrapurpurin when heated, evolving a large quantity of red fumes; in one experiment oxalic acid and a nitro-acid were obtained, but no phthalic acid.

*Action of Ammonia.* When an ammoniacal solution is heated to  $100^{\circ}$  in a sealed tube for some hours, its purple colour changes to indigo-blue, and the solution acidified with hydrochloric acid deposits a dark purple precipitate, probably isomeric with Stenhouse's purpuramide or purpurein, which dissolves in ammonia and in sodium carbonate with a blue colour, in caustic alkalis with a red-purple colour. It dyes alumina-mordants purple, weak iron-mordants indigo-blue.

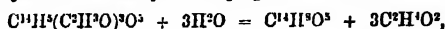
*Metallic Derivatives.* Anthrapurpurin forms metallic derivatives which are insoluble or nearly so in water, except those of the alkali-metals. It dissolves in *potash* and *soda*, producing beautiful violet-coloured liquids, which become blue in the shade when heated. They are not so blue as those obtained with alizarin. The sodium-derivative is difficultly soluble in alcohol. Anthrapurpurin also dissolves in solutions of the alkaline carbonates with a reddish purple colour, and is precipitated by carbonic acid. A solution of sodium bicarbonate, if gently heated, dissolves anthrapurpurin more readily than alizarin. With the chlorides of *calcium*, *magnesium*, *barium*, and *strontium*, the ammoniacal solution of anthrapurpurin gives purple precipitates. Specimens of the barium precipitate dried at  $170^{\circ}$ – $180^{\circ}$ , gave proportions of barium about 2 p. c. lower than that required by the formula,  $C^{20}H^{10}Ba^2O^{18}$ . With alumina anthrapurpurin forms a lake somewhat similar to that produced with purpurin. *Cupric acetate* added to an alcoholic solution of anthrapurpurin changes it from yellow to a beautiful purple, which cannot be distinguished from that produced with alizarin under the same circumstances. When boiled with *alum* or *sulphate of alumina*, it does not give any special reaction, whereas its isomeride, purpurin, gives a pink solution which is fluorescent. In basic aluminium sulphate, however, it dissolves to some extent, forming an orange-pink solution, which is not fluorescent; acids precipitate the colouring matter from this solution.

*Dibromanthrapurpurin.*—When anthrapurpurin is digested with bromine and carbon disulphide for several hours in a flask connected with an inverted condenser, the excess of these substances then driven off, and the residue crystallised from glacial acetic acid, an orange-coloured product is obtained, giving a percentage of bromine a little higher than that required by the formula of dibromanthrapurpurin,  $C^{18}H^8Br^2O^8$ .

*Triacetyl-anthrapurpurin*,  $C^{20}H^{10}O^8 = C^{14}H^4(C^2H^3O)^3O^8$ . Anthrapurpurin heated under pressure with acetic anhydride in excess to a temperature of  $150^{\circ}$ – $160^{\circ}$  for four or five hours, dissolves entirely, and the solution on cooling deposits a large quantity of pale yellow scales, which are easily purified by draining off the excess of acetic anhydride, and recrystallising three or four times from glacial acetic acid. For the preparation of this compound, it is not necessary to use pure anthrapurpurin, the crude product before treatment with alcoholic caustic soda answering very well; but in this case the product should be recrystallised till the mother-liquors are of a clear pale yellow colour.

The substance thus obtained gave, in two analyses, 62.90 and 62.77 p. c. carbon, 8 and 3.77 hydrogen: numbers which agree best with the formula of a triacetyl-derivative (62.83 C. and 3.66 H.), but nevertheless, approximate closely to those required by the formula of diacetyl-anthrapurpurin,  $C^{18}H^8O^8 = C^{14}H^4(C^2H^3O)^2O^8$ , viz., 3.5 C. and 3.5 H. The true composition of the acetyl-derivative is, however, readily

determined by boiling it with alcoholic potash or soda, whereby it is resolved into acetic acid and anthrapurpurin, and weighing the anthrapurpurin thus obtained. For this purpose, a weighed quantity of the acetylic derivative was boiled for some time with alcoholic soda, until the alcohol had been nearly all driven off; water was then added, and the purple solution boiled until quite free from alcohol; the anthrapurpurin was then precipitated with hydrochloric acid, and after standing for twenty-four hours, was collected on a weighed filter, well washed with cold water, dried at  $110^{\circ}$ , and weighed. As the filtrate contained a small quantity of anthrapurpurin in solution, it was agitated with ether, and the ethereal solution evaporated in a weighed dish. The united weights of the colouring matter on the filter and that extracted from the washings with ether, gave in two experiments 66.61 and 67.21 p. c. anthrapurpurin. Now, the decomposition of triacetyl-anthrapurpurin, according to the equation:—



would yield 67.01 of anthrapurpurin, a number closely agreeing with experiment, whereas a diacetyl-derivative similarly decomposed would give 75.3 p. c. This substance is therefore triacetyl-anthrapurpurin.

Triacetyl-anthrapurpurin melts at  $220^{\circ}$ – $222^{\circ}$ . It is not very soluble in alcohol, but moderately so in glacial acetic acid. It crystallises from this latter solvent in beautiful pale yellow glistening scales; as already mentioned, it decomposes when heated with alkalis.

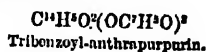
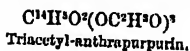
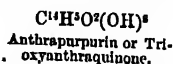
When added gradually and in small quantities at a time to nitric acid, sp. gr. 1.5, triacetyl-anthrapurpurin dissolves without effervescence, forming a dark yellow solution; this, on being slowly added to a large quantity of cold water, deposits a pale brown precipitate, which, when collected and washed, dissolves in potash with a reddish purple colour. This solution does not appear to give any bands when viewed by the spectroscope, but a considerable absorption in the orange and violet. The addition of acid causes the colouring matter to separate as an orange precipitate. This substance dyes alumina-mordants of an orange colour, and weak iron-mordants of a reddish-purple.

*Tribenzoyl-anthrapurpurin*,  $C^{16}H^2O^3 = C^{14}H^2(C^2H^3O)^2O^3$ , is formed by boiling anthrapurpurin with benzoyl chloride. Hydrochloric acid is then evolved, the anthrapurpurin dissolves, and the product on cooling forms a viscid mass, which may be purified by repeated boiling with water, and crystallisation from glacial acetic acid. This latter operation must be repeated, and after a portion of the substance, which first separates as a yellow powder, has been filtered off, the mother-liquor gradually yields small rosette-shaped groups of dark yellow or brownish crystals, which under the microscope, appear well formed and transparent.

The substance thus purified gave by analysis 73.6 to 73.72 p. c. carbon and 3.6–3.68 hydrogen, the formula above given requiring 73.94 p. c. carbon and 3.53 hydrogen. A dibenzoyl-derivative would require 72.75 carbon and 3.45 hydrogen.

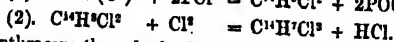
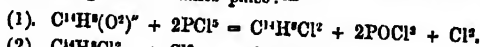
Tribenzoyl-anthrapurpurin melts at  $183^{\circ}$ – $185^{\circ}$ , dissolves with moderate facility in boiling glacial acetic acid, and is decomposed by alcoholic potash.

The composition of these acetyl and benzoyl derivatives shows that anthrapurpurin may be regarded as anthraquinone in which 3 at. H. are replaced by 3 at. HO. This compound and its derivatives may therefore be formulated thus:—



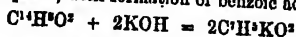
**ANTHRAQUINONE**,  $C^{14}H^2O^2$ .—The boiling point of this compound is above that of mercury. Its vapour-density, determined by Deville a. Troost's method, is 7.33; by calculation 7.20 (Graebe, *Deut. Chem. Ges. Ber.* v. 15).

*Action of Phosphorus Pentachloride*.—On heating anthraquinone with phosphorus pentachloride (diluted with phosphorus oxychloride) in sealed tubes for some hours to  $190^{\circ}$ – $200^{\circ}$ , the following reaction takes place:—



The trichloranthracene thus obtained is not pure, but always contains more highly chlorinated products (Graebe a. Liebermann, *Ann. Ch. Pharm.* clx. 121).

*Action of Alkalis*.—When anthraquinone is heated for some time with caustic potash to  $250^{\circ}$ , it is decomposed, with formation of benzoic acid:—



(Graebe a. Liebermann, *loc. cit.*). According to Wartha (*ibid.* clxi. 305) the fusion of

anthraquinone with potash gives rise to the formation of alizarin. When anthraquinone is heated with potassium hydrate and water, an alcoholic solution of anthraquinone then added, and the heating continued, with constant stirring, a green colour is first produced which finally passes into the purple-blue of potassium-alizarin; and on dissolving the fused mass in water and adding hydrochloric acid, alizarin is precipitated, and may be extracted by ether. The quantity obtained is, however, but small, as the alizarin is partly decomposed by the excess of alkali present.\* A larger product is sometimes obtained by mixing the anthraquinone with sodium or potassium ethylate before adding it to the fused potash.

**Nitro-anthraquinones** (Böttger a. Petersen, *Deut. Chem. Ges. Ber.* iv. 226; Liebermann, *ibid.* 230; Peterson, *ibid.* 301).—These bodies cannot be obtained directly from anthraquinone by the action of nitric acid; but by oxidising anthracene with nitric acid, there is obtained, together with anthraquinone, a dinitroanthraquinone identical with Anderson's dinitro-oxanthracene and Fritzsche's oxydinitrophenone.

The nitration of anthraquinone is however readily effected by a mixture of concentrated sulphuric and nitric acids. The product is a dinitroanthraquinone which separates, on pouring the acid mixture into water, in yellowish-white flocks, insoluble in water, difficultly soluble in alcohol and benzene, still less soluble in ether, and crystallising from these solvents in minute monoclinic, almost colourless crystals. At about 252° it cakes together to a brown mass, from which, at higher temperatures, with partial decomposition of the residue, yellow to brown needle-like crystals sublime. This body forms crystalline double compounds with various hydrocarbons. It does not yield with anthracene the fine violet compound given by Fritzsche's 'reagent' (*1st Suppl.* 215). On fusion with potassium hydrate, it yields alizarin in considerable quantity, a proof that the two nitro-groups occupy the same positions as the two OH

groups do in alizarin; that is to say, that its rational formula is  $C^{11}H^4 \left( \frac{H^1}{(O^2)^2} \right)^2 \left( H^2(NO^2)^2 \right)^2$  (*ibid.* 215).

**Action of Sulphuric Acid on Dinitro-anthraquinone.**—When dinitro-anthraquinone is dissolved in excess of strong sulphuric acid (about 1 part in 18 parts), and the mixture is heated on a sand-bath at about 200°, a moderate evolution of sulphurous anhydride takes place, the brown-yellow liquid becoming deep brown-red. When the reaction becomes more violent, the source of heat is removed, the whole being afterwards heated again slowly, until the evolution of sulphurous anhydride ceases. The mass is then poured into cold water; the precipitated dark brown-red flocks are well washed, repeatedly dissolved in dilute alkali, reprecipitated by acid, and finally dissolved in alcohol; and the solution is slowly evaporated. The exceedingly stable now colouring matter, which can also be obtained by treating anthraquinone with a mixture of sulphuric and nitric acids (16 to 18 parts conc. sulphuric and 1 part nitric acid, sp. gr. 1.5), is slightly soluble in water, forming a peach-coloured solution; readily soluble in alcohol, ether, acetic ether, and chloroform; less soluble in benzene, with a magnificent red violet colour. It separates from these solvents, on slow evaporation, as a violet-red crystalline-granular mass; on quick evaporation, in violet-brown, metallic-glistening crusts. Cotton is dyed violet by it without the use of mordants. When heated, it melts, but only a small portion sublimes unchanged. Its analysis leads to the formula  $C^{14}H^4N^2O^4$ . On fusion with potassium hydrate, ammonia is evolved, but no alizarin could be detected. On treatment with zinc and sulphuric acid, gradual decolorisation and decomposition took place (Böttger a. Petersen).

Liebermann is of opinion that this compound was not obtained pure. He finds that when heated with water to 200°, it is converted into a spongy aggregate of dark needle-shaped crystals, which may be sublimed, but with considerable loss by carbonisation. Metallic-green shining needles are thus obtained, very much like naphthazarin. They contain nitrogen, though not in very considerable quantity. The vapour of this body strikingly resembles that of indigo.

According to Petersen (*Deut. Chem. Ges. Ber.* iv. 301), the violet body formed by treating dinitroanthraquinone with concentrated sulphuric acid, is di-imido-hydroxyl-anthraquinone,  $C^{14}H^4N^2O^4$ . On passing nitrous acid into its solution in alcohol and ether, oximido-dihydroxyl-anthraquinone,  $C^{14}H^4NO^3$ , is formed, which by sublimation is obtained in yellow or hyacinth-red, flat, feathery needles, which dissolve in caustic alkalis with a raspberry colour, and when fused with caustic potash, give alizarin. When this body is dissolved in concentrated nitric acid,

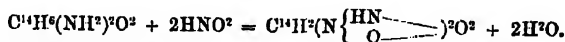
\* Graebe a. Liebermann did not obtain alizarin by fusing anthraquinone with potash, probably on account of this further decomposing action.

dinitro-dihydroxyl-anthraquinone is obtained, which, on the addition of water, separates in yellow, very electric flakes, dissolving in caustic potash with a violet colour.

The formation of the oximido-compound corresponds with that of oximido- $\alpha$ -naphthol which Graebe and Ludwig obtained by the same reaction from di-imido- $\alpha$ -naphthol.

**Diamidanthraquinone**,  $C^{14}H^6(NH^2)^2O^2$ , is easily formed by reduction of dinitro-anthraquinone with sodium sulphhydrate (Böttger a. Petersen), or with tin and hydrochloric acid (Liebermann). It separates in the form of a red powder more or less soluble in alcohol, ether, acetic ether, and other solvents. According to Böttger a. Petersen, it dissolves easily in acids, especially when concentrated; according to Liebermann only in concentrated acids. It melts at  $236^\circ$ , and sublimes even at lower temperatures in magnificent garnet-red flat needles, with a greenish reflex, often united in feathery groups (B. and P.); in long capillary needles (L.). From alcohol and ether it crystallises in small needles (B. and P.); crystallises well from benzene (L.). It does not yield any colouring matter when heated with strong sulphuric acid (L.). According to Böttger a. Petersen it yields alizarin when fused with potash; but according to Liebermann, the colouring matter thus obtained differs in some respects from alizarin, especially in the manner in which it sublimes, and its behaviour when its solution in potash is exposed to the air.

When a solution of diamidanthraquinone in concentrated acid is treated with nitrous acid, an azo-derivative is formed, but it remains for the most part in solution, and is decomposed, with reproduction of anthraquinone, by the continued action of nitrous acid. But by acting with nitrous acid on diamidanthraquinone dissolved in common ether or in ethyl acetate, a peculiar azo-derivative is formed, which separates out on passing a current of the gas through the liquid, as a delicate brownish-violet powder, extremely alterable, and decomposed with slight detonation at about  $68^\circ$ , a bulky residue of carbon remaining. Analyses of several preparations led to the formula  $C^{14}H^6N^4O$ . It is soluble in alcohol and water, with a beautiful violet colour. When heated or left to stand for some time, both the aqueous and alcoholic solutions are decomposed, with reproduction of diamidanthraquinone, which falls down, together with a brown decomposition-product, accompanied by but a slight evolution of nitrogen. Böttger a. Petersen look upon this compound as a dinitroso-amidanthraquinone containing twice the univalent group,  $N \begin{Bmatrix} H \\ NO \end{Bmatrix}$ , or, in accordance with Graebe and Ludwig's observations on certain naphthol-derivatives, as a dioximido-amidanthraquinone containing twice the univalent group,  $N \begin{Bmatrix} HN \\ O \end{Bmatrix} > O^2$ , and express the reaction by the equation:—



By fusion with potassium hydrate it yields alizarin, according to Böttger a. Petersen, or according to Liebermann the body resembling alizarin which is obtained by similar treatment of diamidanthraquinone. When boiled with aqueous potash it yields a yellow solution, indicating that only a partial conversion of the amidogen-groups has been effected by the nitrous acid (Liebermann).

**Oxyanthraquinones.** *Monooxyanthraquinone*,  $C^{14}H^6O^3 = C^{14}H^5O^2(OH)$ , is formed by the action of melting potash on monobromanthraquinone or anthraquinone-monosulphonic acid; also, according to Liebermann, as a bye-product in the manufacture of alizarin (by fusing anthraquinone-disulphonic acid with potash). It may be separated from alizarin by its solubility in baryta-water, and precipitated from the solution by hydrochloric acid. When purified by sublimation and by crystallisation from acetic acid, it forms yellow needles. It dissolves in alkalis with red-brown colour, but does not give colours with mordants: with lead acetate it forms a bright yellow precipitate. By fusion with potash it is converted into alizarin, the change taking place by assumption of an atom of oxygen (Liebermann, *Deut. Chem. Ges. Ber.* iv. 103; v. 868).

Liebermann regards this compound as identical with anthraflavic acid, which, according to Perkin, on the contrary, is a dioxyanthraquinone isomeric with alizarin. Perkin has, however, pointed out that the two compounds are probably formed together in the manufacture of alizarin, and are separated by treatment with baryta-water, in which the dioxyanthraquinone is insoluble (see p. 87).

*Acetyl-monooxyanthraquinone*,  $C^{14}H^5O^2(OC^2H^3O)$ , produced by heating oxyanthraquinone to  $100^\circ$  with acetic anhydride, crystallises from alcohol in very small, nearly colourless fatted needles, melting at  $158^\circ$  (Liebermann).

**ANTHRAQUINONE, ISOMERIDE OF. PHENANTHRENE-QUINONE**,  $C^{18}H^{10}O^2$  (Graebe, *Deut. Chem. Ges. Ber.* v. 861; *Ann. Ch. Pharm.* clxvii. 139. Fittig a. Oster

mayer, *Deut. Chem. Ges. Ber.* v. 933; *Ann. Ch. Pharm.* clxvi. 365). This compound is produced by gently heating phenanthrene with a mixture of 1 part. potassium dichromate, 1½ part sulphuric acid, and 3 parts water. A brisk reaction soon commences and goes on without further application of heat. The product may be freed from a small quantity of anthraquinone, formed by oxidation of admixed anthracene, by partial crystallisation from alcohol, or better from a mixture of equal volumes of glacial acetic acid and water, in both of which solvents it dissolves more easily than anthraquinone (F. and O.). Graebe prepares the quinone by dissolving phenanthrene in hot glacial acetic acid, and gradually adding a solution of chromic acid in acetic acid, so as to keep the liquid just at the boiling point; to complete the reaction the solution must be boiled for some time. On distilling off the greater part of the acetic acid, and adding water to the residue, phenanthrene-quinone separates as a crystalline precipitate, which may be purified by crystallisation from glacial acetic acid, or more conveniently by dissolving it in a solution of acid sodium sulphite and reprecipitating with an acid.

Phenanthrene-quinone is almost insoluble in cold water, but dissolves sparingly in hot water, and in cold alcohol somewhat more freely than in boiling alcohol, still more in ether, benzene, and glacial acetic acid. It crystallises in dark reddish-yellow or orange-yellow needles or prisms (Graebe; F. and O.); melts at 198°, and sublimes at a higher temperature, with partial decomposition, in brilliant transparent orange-red plates.

Phenanthrene-quinone heated with bromine to 100° in sealed tubes yields a compound which is but little soluble in ordinary solvents, and appears to be a dibromoquinone.

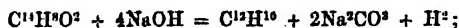
Phenanthrene-quinone dissolves without alteration in cold sulphuric acid, and no sulphonic acid is formed even at 100°; but on heating the solution more strongly, decomposition takes place. The quinone may, however, be converted into sulphonic acids by acting on it with sulphuric anhydride.

Strong nitric acid dissolves phenanthrene-quinone, forming a red solution, from which the quinone is reprecipitated on addition of water. A boiling mixture of sulphuric and nitric acids converts it, but not readily, into nitro-compounds, from which by crystallisation from acetic acid dinitrophenanthrene-quinone  $C^{14}H^8(NO_2)^2O^2$  is obtained, in yellow silky plates.

Phenanthrene-quinone is not reduced by sulphurous acid in the cold, but when heated to 100° with the aqueous acid it is converted into phenanthrene-hydroquinone  $C^{14}H^8(OH)^2$ . By heating with zinc-dust it is reduced to phenanthrene, but the temperature at which the reduction takes place is higher than with anthracene.

By oxidation with chromic acid, phenanthrene-quinone is converted into diphenic acid,  $C^{14}H^{10}O^4$ .

Heated with soda-lime, phenanthrene-quinone is resolved into diphenyl, carbon dioxide and hydrogen:



whereas anthracene similarly treated yields chiefly benzene. These reactions conjoined with others show that the two aromatic nuclei  $C^6H^4$  are linked together directly in phenanthrene, but not in anthracene (see further pp. 94, 95).

*Compounds of Phenanthrene-quinone with Alkaline Bisulphites.*—The sodium salt  $C^{14}H^8O^2 \cdot NaHSO^3 + 2H^2O$ , or probably  $C^{14}H^8 \begin{Bmatrix} OH \\ OSO^3Na \end{Bmatrix} + 2H^2O$ , is formed by dissolving the quinone in a warm solution of acid sodium sulphite; and crystallises in small colourless plates. It is slowly decomposed by water, quickly by acids and alkalis; when exposed to the air, it absorbs oxygen, and sulphuric acid is formed. The potassium salt is a very similar body.

*Phenanthrene-hydroquinone*,  $C^{14}H^8(OH)^2$ , is produced by the action of sulphurous acid on the quinone, the reduction taking place slowly even in the cold. This is one of the distinguishing reactions between phenanthrene-quinone and anthraquinone, which latter is not acted on by sulphurous acid. When phenanthrene-quinone is heated to 100° with excess of aqueous sulphurous acid, it dissolves, and the solution on cooling deposits the hydroquinone in long colourless needles. An alcoholic solution of sulphurous oxide reduces the quinone still more readily.

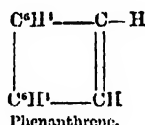
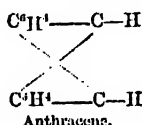
Phenanthrene-hydroquinone in the moist state absorbs oxygen, but when dry it is more stable. By boiling with water in an open vessel, it is first converted into a brownish-black quinhydrone, and then into the quinone. The same reaction takes place when it is acted on by ferric chloride, nitric acid, chromic acid, &c. When the hydroquinone is dissolved in caustic potash, and the solution is exposed to the air, a green precipitate is formed, which gradually changes into the quinone. This green

compound, which is coloured brown by acids and green again by alkalis, probably consists of the potassium salt of phenanthrene-quinhydrone; it is also formed by dissolving phenanthrene in ammonium or potassium sulphide, or in caustic soda, with the aid of zinc-dust, and exposing these solutions to the air (Graebe, *Ann. Ch. Pharm.* clxvii. 146).

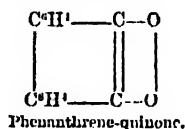
*Diacetyl-phenanthrene-hydroquinone*,  $C^{14}H^{10}(C^2H^3O)^2O^2$ , is produced by heating phenanthrene-hydroquinone with acetic anhydride to  $140^{\circ}$ – $180^{\circ}$ . It crystallises from hot benzene in colourless plates, melting at  $202^{\circ}$ . It is a very stable compound, which is not oxidised by boiling with solution of potassium dichromate and sulphuric acid, but a solution of chromic acid and acetic acid converts it into the quinone. It is not altered by heating with caustic potash of sp. gr. 1.3, but on concentrating the liquid, decomposition takes place, and water added to the solution throws down the green body above mentioned (Graebe).

*Constitution of Anthraquinone and Phenanthrene-quinone.*

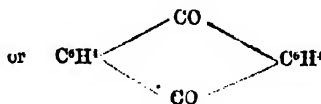
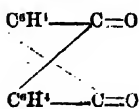
The synthesis of anthracene from benzyl-toluene (p. 82), and that of phenanthrene from stilbene show that the two aromatic nuclei contained in the former are disconnected, whereas in the latter they are linked together; and this conclusion is corroborated by the fact that phenanthrene, when heated with soda-lime, yields diphenyl, whereas anthracene yields chiefly benzene. These two isomeric aromatic hydrocarbons may accordingly be represented by the formulæ:



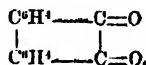
According to Graebe's theory, therefore, which represents the quinones as containing two atoms of oxygen linked together so as to form a diatomic group, the corresponding quinones should be represented by the formulæ:



Fittig & Ostermayer, on the other hand, regard the quinones, not as compounds containing the diatomic group ( $O^2$ ), but as double ketones, in which the oxygen-atoms are not linked together, but each is united to a carbon-atom by two units of affinity; anthraquinone being, according to this view,

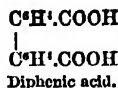
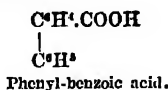


and phenanthrene-quinone,

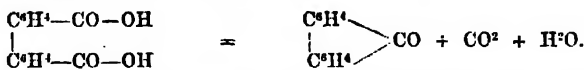


They find that phenanthrene-quinone is converted by oxidation with chromic acid into diphenic acid,  $C^{14}H^{10}O^4$ , and that this acid, when heated with excess of quicklime yields, not diphenyl,  $C^{12}H^{10}$ , but diphenylene-ketone,  $C^{12}H^8O$ . This ketone, fused with potash, is converted into phenyl-benzoic acid,  $C^{13}H^{10}O^2$ , and when the calcium salt of this acid is heated with quicklime, the ketone is regenerated, and a small quantity of diphenyl,  $C^{12}H^{10}$ , is produced, which may be obtained in larger quantity by heating the calcium salt without quicklime.—The formation of

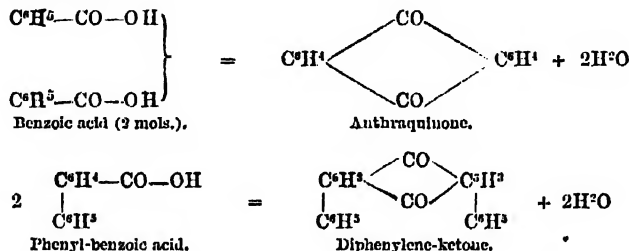
diphenyl in this manner shows that phenyl-benzoic acid and diphenic acid are constituted as follows:—



The formation of diphenylene-ketone from diphenic acid is exactly analogous to that of dimethyl-ketone (acetone) from acetic acid:



Fittig a. Ostermayer, however, regard it as more probable that the molecular formula of this ketone is  $\text{C}^{20}\text{H}^{16}\text{O}_2$ . Kekulé has lately shown (*Deut. Chem. Ges. Ber.* v. 908) that on heating calcium-benzoate, a small quantity of anthraquinone is formed, and Jaffé (*ibid.* iii. 694), as well as Barth a. Sennhofer (*Ann. Ch. Pharm.* clxiv. 109), has found that di- and tri-oxybenzoic acids are easily converted into derivatives of anthracene. Now, phenyl-benzoic acid behaves in a similar manner, as shown by the following equations:—



Diphenylene ketone is therefore diphenyl-anthraquinone; when fused with potash, it again yields phenyl-benzoic acid, just as anthraquinone is resolved by this reaction into 2 molecules of benzoic acid (Fittig a. Ostermayer).

On the other hand, it may be observed that the constitution of diphenylene ketone as diphenylated anthraquinone may be represented on Graebe's view of the constitution of the latter compound, and of quinones in general, as well as by that of Fittig and Ostermayer, namely by the formula,



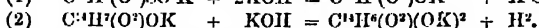
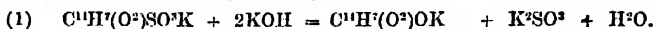
With regard to the constitution of quinones in general, Graebe observes (*Ann. Ch. Pharm.* clxvii. 163), that, although the formation of anthraquinone by heating calcium benzoate, as well as the formation of rufsallic acid and of anthrachrysone, and the behaviour of anthraquinone and phenanthrene-quinone when fused with potash or heated with lime, may perhaps be more simply explained on the supposition that the quinones are double ketones,—nevertheless, there are other facts which directly contradict this view, and show that these bodies actually contain the bivalent group (O—O)', capable of replacing and being replaced by 2 atoms of hydrogen, chlorine, &c., whereas if the 2 oxygen-atoms were not thus linked, they would be equivalent to 4 atoms of a monatomic radicle. The quinones are, in fact, produced by replacing 2 atoms of hydrogen by 2 of oxygen, whereas in the formation of ketones 2 atoms of hydrogen are replaced by only 1 atom of oxygen. Moreover, ketones take up 2 atoms of hydrogen for each atom of oxygen which they contain, and are thereby converted into secondary alcohols, whereas quinones take up only 1 atom of hydrogen for 1 of oxygen, and are converted into hydroquinones.

**ANTHRAQUINONE-SULPHONIC ACIDS** (Graebe a. Liebermann, *Ann. Ch. Pharm.* clx. 121).

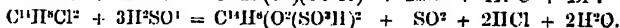
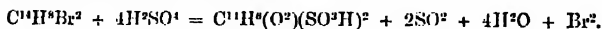
1. *Anthraquinone-monosulphonic Acid*, or *Sulphanthraquinonic Acid*,  $\text{C}^{14}\text{H}^8(\text{O})_2\cdot\text{SO}_3\text{H}$ , produced by heating 1 part of anthraquinone and 2-3 parts sulphuric acid to  $250^\circ\text{--}260^\circ$ .

The pure acid is best obtained by decomposing the lead or barium salt with sulphuric acid. It forms yellow scales, and is readily soluble in water and alcohol, but nearly insoluble in sulphuric acid. The *barium salt*  $[C^{14}H^8(O^2)SO^2]_2Ba + H^2O$  forms indistinct yellow crystals, sparingly soluble in cold and a little more readily in hot water. The *calcium salt* has also a yellow colour, and is much more soluble in water. The *sodium salt* forms indistinct yellow crystals, and gives with water a yellowish red solution.

On heating the potassium salt with caustic potash and a little water, the mass gradually assumes a violet colour; and if the heat has been sufficiently high, it contains alizarin, formed according to the equations:—



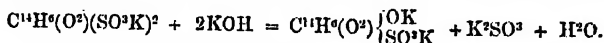
2. *Anthraquinone-disulphonic Acid*,  $C^{14}H^8(O^2)(SO^2H)^2$ , is formed by heating anthraquinone with 4-5 parts of sulphuric acid to  $270^\circ$ - $280^\circ$ . It may also be formed directly from anthracene, namely by heating dichlor- or dibrom-anthracene with a mixture of concentrated and fuming sulphuric acid:



(Graebe & Liebermann, *Deut. Chem. Ges. Ber.* iii. 636). According to Perkin (*Chem. News*, xxii. 37), dichloranthracene dissolves in fuming sulphuric acid, forming *dichloranthracene-monosulphonic acid*  $C^{14}H^8Cl^2(SO^2H)$ , and *dichloranthracene-disulphonic acid*  $C^{14}H^8Cl^2(SO^2H)^2$ . Dibromanthracene yields corresponding products. The disulpho-acids, treated with oxidising agents, exchange their bromine or chlorine for oxygen, forming anthraquinone-disulphonic acid.

This acid crystallises from an aqueous solution in yellow crystals, and is less soluble than the monosulpho-acid. It is nearly insoluble in sulphuric acid. Its yellow salts dissolve in water with a yellowish-red colour, and do not crystallise well. The *barium salt* is very sparingly soluble in cold water, but a little more readily in hot water; the *calcium salt* is also not very soluble.

On heating one of the salts with potash or soda, alizarin is produced, the formation of which, however, takes place by two stages: First, the red colour of the mixture gradually changes to a dark blue, the potassium salt of an oxyanthraquinone-sulpho-acid being formed:



On dissolving some of the dark blue mass in water, and adding dilute sulphuric acid, sulphur dioxide is evolved, and the blue colour of the liquid changes into yellow, but no precipitate is formed.

On heating the blue mass longer, its colour becomes more and more purple, alizarin being now formed, which is obtained as a yellowish red precipitate on adding an acid to the solution of the fused mass. It is easy to find the point when most of the intermediate product is decomposed, by shaking the acid solution with ether, which dissolves only the alizarin, whilst the oxyanthraquinone-sulphonic acid remains in the aqueous solution. On adding an alkali to the latter, the intensity of the blue colour shows whether there is still any of this acid present or not. The crude alizarin obtained by this process always contains some oxyanthraquinone and other colouring matters, which modify the colours produced on mordanted cloth. Moreover, a small quantity of anthraquinone is generally formed by reduction,  $SO^2H$  being replaced by hydrogen; this reduction is more readily effected by heating the sulpho-acids with quicklime, whereupon anthraquinone sublimates in considerable quantity.

When dichlor-anthracene and dibromanthracene are acted upon by sulphuric acid, sulpho-acids are formed, which when heated are converted into anthraquinone-disulphonic acid, as already observed by Perkin (*1st Suppl.* 179).

*Oxyanthraquinone-sulphonic Acid*,  $C^{14}H^8(O^2)\left\{ \begin{matrix} OH \\ SO^2H \end{matrix} \right\}$ —To prepare this compound, the mixture of potash and anthraquinone-disulphonic acid is heated till the formation of alizarin begins.

After cooling, it is dissolved in water, hydrochloric acid is added, and the liquid filtered. On adding barium chloride to the filtrate, the yellow barium salt of the sulpho-acid separates out, either at once or after evaporation. On decomposing this salt with dilute sulphuric acid, and evaporating the solution, the free acid is obtained in yellow crystals, soluble in alcohol, but not in ether. It forms two series of salts; on dissolving it in caustic potash, a deep blue solution is obtained containing the



compound  $\text{C}^{\text{H}}(\text{O}^{\text{H}})\left\{\begin{smallmatrix} \text{OK} \\ \text{SO}^{\text{H}} \end{smallmatrix}\right.$ ; on adding hydrochloric acid to this solution, it assumes a yellowish-red colour, the salt  $\text{C}^{\text{H}}(\text{O}^{\text{H}})\left\{\begin{smallmatrix} \text{OH} \\ \text{SO}^{\text{H}} \end{smallmatrix}\right.\text{K}$  being formed. The acid barium salt, which has been already mentioned, is moderately soluble in boiling water, but only sparingly in cold water, and still less in dilute hydrochloric acid. Its yellowish-red solution, like those of the other salts of this acid, becomes yellow on addition of hydrochloric acid, and gives with baryta-water a blue precipitate,  $\text{C}^{\text{H}}(\text{O}^{\text{H}})\left\{\begin{smallmatrix} \text{O} \\ \text{SO}^{\text{H}} \end{smallmatrix}\right.\text{Ba}$ .

**ANTIMONY.** *Estimation and Separation.*—When a neutral and concentrated solution of antimonious chloride is mixed with a slight excess of *gallic acid*, the whole of the antimony is separated as insoluble antimonious gallate. This reaction may be utilised for the estimation of antimony, and for the separation of antimony from tin, arsenic, and other metals.

The above mentioned combination of antimony with gallic acid is insoluble in a neutral or slightly acidulated liquor, but dissolves readily in more concentrated solutions of hydrochloric acid; it is necessary, therefore, for the success of the analysis, that the solution be concentrated by evaporation, and any large excess of acid volatilised. The precipitate is somewhat bulky, but settles rapidly. It cannot, however, be washed on a filter, since it invariably passes through the filter as soon as the acidulated mother-liquor has been washed away; the mixed mode of decantation and filtration must, therefore, be resorted to, which in this particular instance presents neither inconvenience nor difficulty.

Antimonious gallate dried at  $100^{\circ}$  has the composition  $\text{Sb}^{\text{O}}\text{O}^{\text{H}}(\text{C}^{\text{H}}\text{H}^{\text{O}})^2 + 3\text{H}^{\text{O}}$ , and contains 40.85 p. c. of metallic antimony. It is exceedingly hygroscopic.

The antimony may either be weighed in the form of antimonious gallate, as the composition of the precipitate is perfectly definite, or the salt may be dissolved in hydrochloric acid, and the antimony precipitated by sulphuretted hydrogen in the usual way.

Solutions of antimonious chloride are unfit for the estimation of this metal by gallic acid; they must, therefore, before precipitation, be reduced to the state of antimonious chloride. This reduction is readily effected by mixing the slightly acidulated solution of antimonious chloride with a solution of potassium iodide, when the following reaction ensues—



The iodine and excess of acid having been removed by evaporation, the solution is ready to be precipitated by gallic acid.

*Separation of Antimony from Arsenic.*—Potassium iodide, which in presence of hydrochloric acid reduces antimonious chloride to the state of antimonious chloride, with evolution of iodine, reacts in a similar manner upon arsenic acid, which it reduces to arsenious acid—



This reaction greatly facilitates the separation of the two metals. The antimony is estimated by gallic acid in the manner already described, and the arsenic is precipitated subsequently by sulphuretted hydrogen.

*Separation of Antimony from Tin.*—Potassium iodide has no reducing effect upon stannous chloride, but when an excess of iodide is introduced into the solution, a double decomposition takes place, and the liquid consists of a hydrochloric acid solution of stannous iodide. Gallic acid separates antimony from stannous iodide much more readily than from the stannous chloride. If the quantity of potassium iodide employed has been properly adjusted, the antimonious gallate settles very rapidly down; on the contrary, when the operation has been badly conducted, the antimonious gallate is mixed with stannous oxide, and the whole remains in suspension without subsiding. In this case the liquid should be rejected as unfit for a successful operation.

The separation of antimony from arsenic and tin together may also be effected in a manner similar to the separation of antimony from tin; but the results hitherto obtained are not very satisfactory (Hugo Twinn, *Chem. News*, xxiv. 207, 221). See further *Antimony and Tin*.

In the precipitation of antimony from solutions containing tin by metallic iron, according to Tooke's method (1st Suppl. 182), Attfield finds that the quantity of antimony obtained is too small, if the air has exerted an oxidising action on the ferrous salt produced in removing the excess of iron. The cause of the loss is that metallic antimony is soluble in ferric chloride. Hence, in determining antimony by this method,

2nd Sup.

H

it is necessary to exclude the air till the whole of the iron-salt is removed, which may for the most part be effected by adding hot de-aerated water immediately after the iron is dissolved and decanting rapidly; in exact experiments, however, it is necessary to surround the vessel with an atmosphere of carbon dioxide (*Pharm. J. Trans.* [2] x. 512).

**Hydride of Antimony, or Stibine,  $\text{SbH}_3$ .** This compound acts on fused antimonious chloride in such a manner that antimony is separated and hydrogen sulphide given off. Phosphoric chloride is but slightly attacked by it with formation of phosphorous chloride, antimonious chloride, and hydrogen chloride. On phosphorous chloride and stannic chloride stibine does not act.

**Oxides.** On the isodimorphism of antimonious oxide and arsenious oxide, see ARSENIC (p. 104).

Antimonious oxide dissolves easily in aqueous sodium sulphide, forming a liquid of the colour of chlorine-gas, from which hydrochloric acid precipitates antimony trisulphide, without separation of sulphur (Unger, *Arch. Pharm.* [2] cxlvii. 193).

**Antimonious Hydrate.** By precipitating a solution of potassium antimonate with nitric acid, washing the precipitate, and leaving it to itself during a whole summer, Geuther (*Jenaische Zeitschr.* vii. 121) has obtained a hydrate having the composition  $\text{HSbO}_3$  or  $3\text{H}_2\text{O} \cdot \text{Sb}_2\text{O}_3$ . When heated to  $175^\circ$ , it gives off 2 mol. water and is transformed into the monohydrate,  $\text{HSbO}_3$  or  $\text{H}_2\text{O} \cdot \text{Sb}_2\text{O}_3$ .

**Sodium antimonate** differs in composition according to its mode of preparation. By precipitating the product of the action of potash-solution on native antimony trisulphide with soda-solution, the well known compound  $\text{Na}_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$  is obtained.

a. By boiling the filtrate from this compound with sulphur,  $\text{Na}_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  was obtained. b. By boiling antimony ore with potash-solution and sulphur, and precipitating with soda-solution,  $6\text{Na}_2\text{O} \cdot 5\text{Sb}_2\text{O}_3 \cdot 33\text{H}_2\text{O}$  was formed. This salt is also produced when the hydrochloric acid solution of sodium antimonate (which separates from the mother-liquors obtained in making Schlippe's salt) is treated with tartaric acid, diluted with water, and precipitated by soda-solution in excess. The solution of this latter salt scarcely alters the colour of litmus. The salt itself is difficultly soluble in pure water; a solution was obtained by long washing on the filter, containing in 100 grams, 0.085 gram of the salt. Sodium antimonate dissolves but slowly in aqueous sodium sulphide, even on warming; in time, however, a large amount is taken up. From the almost colourless solution, the golden sulphide  $\text{Sb}_2\text{S}_3$  is precipitated by acids without admixture of free sulphur, showing that sulphantimonate of sodium has been formed (Unger, *Arch. Pharm.* [2] cxlvii. 193).

A hydrated calcium antimonate,  $3\text{CaO} \cdot 2\text{Sb}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , occurs on the calcareous matrix of non-arseniferous ullmannite  $\text{NiS} \cdot \text{NiSb}_2$ , at Waldenstein in Carinthia, partly as a greenish earthy mass, partly in pseudomorphous crystals of the regular system, exhibiting the combination  $\infty \text{O} \infty \cdot \text{O} \infty \text{O}$ . Its formation appears to be due to the mutual action of the ullmannite and the matrix (Rumpf, a Ullik, *Jahrbuch f. Mineralogie*, 1870, 355).

On antimonate and antimonite of lead from the province of Constantine in Algeria, see NADORITE.

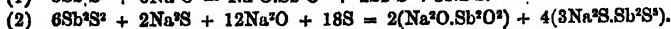
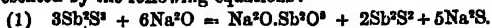
**Oxychlorides.**—By treating antimonious chloride with various proportions of water, compounds are obtained corresponding with the formulae  $\text{SbClO}$  and  $\text{Sb}_2\text{ClO}_3$ . The former of these compounds exhibits two modifications, amorphous and crystalline. The amorphous variety is obtained by treating the chloride with three times its weight of water; the crystalline variety by adding 7 parts water to 10 parts of antimonious chloride, and leaving the mixture to itself for a few days.

The compound  $\text{Sb}_2\text{O}_3 \cdot 2\text{SbClO}$  is obtained when the trichloride is treated with 5 to 60 parts of water; when cold water is used it crystallises in oblique prisms having a silky lustre (Sabanejew, *Zeitschr. f. Chem.* [2] vii. 204).

W. C. Williams (*Chem. News*, xxiv. 224), by heating 1 mol. antimony pentoxide with 3 mol. of the pentachloride to  $140^\circ$  in a sealed tube, has obtained two crystalline oxychlorides: one melting at  $85^\circ$  and having the composition  $\text{Sb}_2\text{Cl}_3\text{O}$ , the other melting at  $97.5^\circ$ , and consisting of  $\text{Sb}_2\text{Cl}_3\text{O}$ . The simple oxychloride  $\text{SbClO}$ , analogous to  $\text{PClO}$ , was not produced.

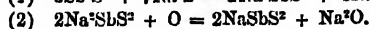
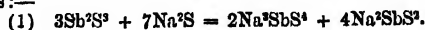
**Sulphides. Trisulphide or Antimonous Sulphide.**—When black antimonous sulphide is treated with potash-solution, and the liquid filtered from the resulting 'crocus' is mixed with caustic soda, sodium antimonate is precipitated, and a liquid is obtained, which Unger supposes to contain a bisulphide of antimony,  $\text{Sb}_2\text{S}_3$ , analogous to realgar, dissolved in aqueous sodium sulphide. This liquid, treated with the necessary amount of sulphur, yields a further quantity of sodium antimonate.

together with a considerable proportion of Schlippe's salt. The two reactions are represented by the following equations:—



When very finely-pounded black antimonious sulphide and a little strong solution of sodium sulphide are rubbed together and warmed to  $20^{\circ}$ – $30^{\circ}$ , a paste is formed, having a fine copper lustre, and from this a body may be obtained having almost the appearance of metallic copper, and the composition  $\text{Na}^2\text{Sb}^2\text{S}^{12} + 2\text{H}^2\text{O}$ , or, according to Unger,  $\text{Na}^2\text{S}.\text{Sb}^2\text{S}^3.2\text{H}^2\text{O} + 3\text{Sb}^2\text{S}^2$ . When decomposed by an acid, however, it yields only the trisulphide. The mother-liquor of the copper-coloured body treated with an additional quantity of sodium sulphide, yields a considerable quantity of Schlippe's salt.

The reaction of *antimony trisulphide* with sodium sulphide differs according to the relative quantities of the two bodies employed. When the trisulphide is treated with a small quantity of sodium sulphide in concentrated solution, the copper-coloured body already mentioned is formed, and in large quantity if the ingredients are heated together for some time out of contact with the air. But when an excess of sodium sulphide is used, Schlippe's salt is formed, together with a red tarry body, which, by repeated solution in water and evaporation, may be obtained in deep red flocks, having the composition  $\text{NaSbS}^3$ , or  $\text{Na}^2\text{S}.\text{Sb}^2\text{S}^3$ . The oxygen of the air is concerned in the reaction; for when the materials are placed together in a closed vessel, very little Schlippe's salt is formed. The result may be explained, by supposing that a body having the composition  $\text{Na}^2\text{SbS}^2$ , or  $2\text{Na}^2\text{S}.\text{Sb}^2\text{S}^2$ , is first formed, together with Schlippe's salt, and that the former is converted by oxidation into sodium sulphantimonite and caustic soda, thus:—



The precipitate produced when the solution of antimony trisulphide in sodium sulphide is poured into acids is very different from the beautiful penta- and tri-sulphides of antimony produced by the ordinary methods, being of the colour of iron oxide, or kermes: it is very bulky and gelatinous. It appears to be anhydrous, and when once dried, is scarcely at all hygroscopic.

This kermes-coloured precipitate possesses the peculiar property of persistently retaining from 1.5 to 2 p.c. sodium sulphide, in such a manner as to be difficultly decomposable by acids (Unger).

*Crocus of Antimony*, the well-known yellow body formed when antimonious sulphide is treated with caustic alkaline solution (i. 328) has, according to Unger, a somewhat complex constitution. When prepared with potash it remains as an ochre-brown powder if dried at a gentle heat, and if heated more strongly, gives off water, melts with intumescence to a glassy mass, without any sublimation of trisulphide, and has the composition  $3(\text{Sb}^2\text{S}^3.\text{H}^2\text{O}) + 6(\text{K}^2\text{O}.\text{Sb}^2\text{O}^3) + 2\text{Sb}^2\text{O}^3$ .

*2. Pentasulphide*.—According to Fr. Wurtz (*J. Pharm.* [4] xi. 456), this compound, prepared from sodium-sulphantimonate, always contains free sulphur (which may be dissolved out by carbon sulphide); he attributes its occurrence to the fact that the mutual action of sodium carbonate, quicklime, sulphur, and antimony trisulphide, likewise gives rise to sodium thiosulphate, which, when decomposed by hydrochloric acids, yields sulphur. The same fact appears to have been noticed by several other observers (*Jahresb. f. Chem.* 1870, 365).

*Compound of Sulphantimonate and Thiosulphate of Sodium*.—By crystallisation of the red mother-liquors obtained in the preparation of Schlippe's salt, which contain much sodium thiosulphate, a salt is obtained in large crystals, having the composition  $3\text{Na}^2\text{S}.\text{Sb}^2\text{S}^3 + 2(\text{Na}^2\text{O}.\text{S}^2\text{O}^3) + 4\text{H}^2\text{O}$ . If the antimony ore from which the Schlippe's salt is obtained contains arsenic, the double salt will also be arsenical. This salt crystallises in a form different from that of Schlippe's salt, viz., in six-sided rhombic pyramids, very much like potassium sulphate. They have a faint greenish tint, effloresce, but not rapidly, and in time become opaque and brown. Treated with acids, they yield a mixture of golden sulphide with free sulphur, amounting to one-third of the weight of the whole precipitate. The saturated hot solution of this salt first deposits tetrahedrons of Schlippe's salt, and then sodium thiosulphate. The crystals melt when gently heated. This compound is of all known inorganic salts the one which contains the largest number of molecules of water (Unger).

**APATITE.** This mineral appears to be of very frequent occurrence in eruptive rocks, being found in such rocks of the most various character, both chemically and petrographically (*E. Zirkel, Jahrbuch f. Mineralogie*, 1870, 301).

Apatite from Canada, occurring in a bed about 1 m. thick, sometimes in crude

masses of sp. gr. 3.142, sometimes in well-defined six-sided prisms, sp. gr. 3.166, has been analysed by R. Hutton (*Chem. News*, xxi. 150), with the following results:—

	$\text{Ca}^2\text{P}^2\text{O}^8$	$\text{CaF}^2$	$\text{CaCl}^2$	$\text{CaCO}^3$	$\text{Fe}^2\text{O}^3$	$\text{H}^2\text{O}$	Sand
Massive	88.61	7.22	0.06	4.47	—	0.08	0.10 = 98.54
Crystals	90.82	5.70	0.14	0.38	0.40	0.32	0.10 = 97.86

**Iodine and Bromine in Apatite.**—The apatite from the beds in the departments of Lot and of Tarn-et-Garonne gave, when treated with sulphuric acid for the manufacture of superphosphate, violet vapours of iodine. The distillate treated for bromine by Bouis' process, gave only faint traces of that element. This phosphate may perhaps be utilised as a commercial source of iodine (Kuhlmann, *Compt. rend.* lxxvi. 1678).

**ARABIN.** *Acetyl-derivatives.*—Arabin heated with 2 parts of acetic anhydride to  $150^\circ$ , swells up to a mass which, when heated with hot water and with alcohol, yields diacetyl-arabin  $\text{C}^6\text{H}^7(\text{C}^2\text{H}^3\text{O})^2\text{O}^2$ , as an amorphous white powder insoluble in hot water, and yielding soluble arabin by saponification. If an excess of acetic anhydride be used, and the temperature raised to  $180^\circ$ , triacetyl-arabin  $\text{C}^6\text{H}^7(\text{C}^2\text{H}^3\text{O})^3\text{O}$  is obtained, exactly resembling the diacetyl-compound (Schützenberger a. Naudin, *Zeitschr. f. Chem.* [2] v. 264).

**ARITE, or AARITE,** is a nickelliferous mineral found on the Ar Mountain (*Basses Pyrénées*), associated with and intimately disseminated throughout a mixture of petrosilox, chalk, blonde, ullmannite, and galena. It is amorphous, and has the colour of breithauptite. Density 7.19. Analysis gave

R.	As.	Sb.	Ni.	Zn.
1.7	11.5	48.6	37.3	2.4 = 101.5.

These numbers calculate to the formula  $\text{Ni}^2(\text{Sb}; \text{As})$ , which is that of an arseniferous breithauptite (iv. 35). It would appear, therefore, that arite should be considered more as a variety of breithauptite, in the same manner as the nickeline, or copper-nickel, from Allemont, which contains 8 p. c. of antimony, is considered a variety of ordinary nickeline (iv. 36). (Pisani, *Compt. rend.* lxxvi. 230.)

**ARRAGONITE.** On the formation of this variety of calcium carbonate, see CARBONATES.

**ARSENIC.** *Occurrence.*—Arsenic occurs frequently in soils, being introduced therein by the weathering of arseniferous pyrites, or in the refuse from manufacturing operations, &c. With reference to chemico-legal investigations, it is important to observe that arsenic may in this manner be introduced into the earth of cemeteries (Sonnenschein, *Arch. Pharm.* [2] cxliii. 245).

*Purification.*—Metallic arsenic may be freed from the dirty deposit which it acquires by keeping in contact with the air, and restored to its pure metallic lustre, by boiling it with a moderately concentrated solution of potassium dichromate acidulated with sulphuric acid, then washing it with alcohol and ether, and fusing it in glass tubes (Böttger, *J. pr. Chem.* [2] ii. 134).

*Detection.*—On the application of Bottondorff's method of detecting arsenic by means of an acidulated solution of stannous chloride (*1st Suppl.* 216) to pharmaceutical purposes, see Hager (*Pharm. Centrbl.* 1870, 201; *Jahresb.* 1870, 066).

When a person is suspected to have been poisoned with arsenic, and nothing but the skeleton is left for investigation, the arsenic should be looked for especially in the bones of the pelvis and the neighbouring spinal vertebrae. For this purpose the following process is given by Sonnenschein (*Arch. Pharm.* [2] cxliii. 250). The comminuted bones are introduced into a glass tube about 10 mm. in diameter, 1 m. long, and closed at the bottom; and this tube is filled to  $\frac{3}{4}$ ds with strong sulphuric acid, and gently heated in a water-bath, in order to expel the carbonic anhydride contained in the bones, and finally sealed before the blow-pipe. After heating in the water-bath for a week with frequent agitation, the substance of the bone is converted into a gelatinous pulp, which may be examined for arsenic in the ordinary way. It is convenient, however, to combine the qualitative with the quantitative analysis. The metallic sulphide, separated from the solution in sodium sulphide is dissolved in fuming nitric acid, or in a mixture of potassium chlorate and hydrochloric acid; tartaric acid is added, then ammonia in excess; and the clear solution, mixed with a magnesium salt, is left in a warm place for several days. The separated precipitate of ammonio-magnesian arsenate, after drying and weighing, may be used for various experiments with Marsh's apparatus, &c.

*Gravimetric Estimation.*—R. Fuller (*Zeitschr. anal. Chem.* 1871, 41) has examined the methods most frequently employed for the estimation of arsenic.

precipitation as trisulphide, as ammonio-magnesian arsenate, and as uranic arsenate, with the view of determining their relative accuracy.

1. *Precipitation as Arsenious Sulphide*.—By a number of very careful determinations it was found that arsenious sulphide is not perceptibly soluble in water, but that to ensure complete and speedy precipitation of arsenic by sulphuretted hydrogen from a solution of arsenious acid, it is necessary that the solution be strongly acidulated, with hydrochloric acid, for example. If the excess of sulphuretted hydrogen be afterwards expelled by a current of carbonic anhydride, the precipitated arsenious sulphide does not contain any appreciable quantity of free sulphur that can be dissolved out by carbon sulphide. The precipitate may be completely dried at  $100^{\circ}$ , and may be further heated in a current of carbonic anhydride to  $120^{\circ}$ , or even to  $150^{\circ}$ – $160^{\circ}$ , without perceptible loss.

The mixture of arsenious sulphide and free sulphur, obtained by passing sulphuretted hydrogen through an acidulated solution of arsenious acid mixed with ferric chloride, may be completely freed from uncombined sulphur by digestion with carbon sulphide; but the precipitate of arsenious sulphide and sulphur obtained by the action of sulphuretted hydrogen on arsenic acid is more difficult to deal with. If the sulphur is precipitated from a hot solution (at  $75^{\circ}$ ) it becomes very intimately mixed with the arsenious sulphide, in the form of little globules, from which it cannot be completely extracted by ammonia or by digestion in the cold with carbon sulphide. The sulphur may, however, be easily dissolved by removing the precipitate from the filter as completely as possible, and digesting with carbon sulphide in a water-bath.

Good results are likewise obtained by determining the arsenic indirectly in the precipitate produced by sulphuretted hydrogen—after drying till constant and weighing—by oxidation of the sulphur and precipitation as barium sulphate. Oxidation with potassium chlorate and hydrochloric acid generally involves a loss from volatilisation of the arsenic as arsenious chloride. Redfuming nitric acid, however, answers very well, because it boils below the melting point of sulphur. The operation may also be effected after exhausting the sulphide on the filter with ammonia, then filtering and evaporating to dryness.

The method of oxidation in an alkaline solution (KHO) by passing a moderate current of chlorine through a warm solution containing excess of pure alkali, as well as the two other methods, usually gives a little more sulphur; on account of the precipitated barium sulphate retaining, as Fresenius has shown, a little potassium chlorate, chloride or nitrate, especially the latter, which must be removed by fusion of the barium sulphate with sodium carbonate, dissolving the residue in hydrochloric acid, and precipitating again as barium sulphate. It is obvious that the indirect method of estimating the arsenic by determining the sulphur in the precipitate may likewise be controlled by direct estimation as ammonio-magnesian arsenate.

2. *Precipitation as Ammonio-magnesium Arsenate*.—This salt, when dried in a vacuum over sulphuric acid, has the composition  $(\text{NH}_4)\text{MgAsO}_4 + 6\text{H}_2\text{O}$ . After drying at  $100^{\circ}$  it contains  $2(\text{NH}_4)\text{MgAsO}_4 + \text{H}_2\text{O}$ , and on ignition yields magnesium pyro-arsenate,  $\text{Mg}_2\text{As}_2\text{O}_7$ . The temperature should be raised gradually to avoid reduction of arsenic to arsenious oxide by the escaping ammonia, and consequent loss by volatilisation.

Fuller has carefully determined: (1) the solubility of this salt in the various saline and other solvents with which it is brought into contact during precipitation; (2) the best and readiest methods of drying; (3) the best means of converting the arsenious sulphide into arsenic acid in order to estimate it as ammonio-magnesium arsenate.

The experiments on the solubility of the salt led to the following results:—

*Solubility in pure distilled water*.—1 part of the precipitate dried at  $130^{\circ}$  dissolved in 2652, or 1 part of the anhydrous arsenate in 2784 parts of water.

*Solubility in weak ammonia* (1 part of ammonia of .98 sp. gr., diluted with 3 parts of water).—1 part of the salt dried at  $100^{\circ}$  dissolved in 15161, and 1 part of the anhydrous arsenate in 15904 parts of this aqueous ammonia.

*Solubility in a dilute solution of ammonium chloride* (1 part of the salt dissolved in 60 parts of water).—The amount of arsenate dissolved was determined by removing the arsenic as arsenious sulphide, and precipitation of the magnesia in the filtrate by means of sodium phosphate, and weighing as magnesium pyrophosphate. 1 part of the salt dried at  $100^{\circ}$  dissolved in 1321 parts, and of the anhydrous salt in 1336 parts of this dilute solution of ammonium chloride.

*Solubility in a concentrated solution of ammonium chloride* (1 part of the salt in 7 parts of water).—1 part of the arsenate dried at  $100^{\circ}$  required 844.7, and 1 part of the anhydrous salt 882.7 parts of the solution of ammonium chloride.

*Solubility in a solution containing 10 parts of ammonium chloride, 10 parts of ammonia, sp. gr. '96, and 60 parts of water.*—1 part of the arsenate dried at 100° requires 2879, and of the anhydrous salt 3022 parts of this mixture.

*Solubility in a solution of magnesium sulphate* (13·3 parts of the crystallised salt dissolved in a litre of water).—1 part of the arsenate dried at 100° required 2763, and of the anhydrous salt 2900 parts of this solution.

*Solubility in magnesia mixture* (1 part of  $MgSO_4$ , 1 part of  $NH_4Cl$ , 4 parts of ammonia, of sp. gr. '96, and 8 parts of water).—The mixture was diluted with 20 parts of water, and contained 72·58 grams of the crystallised magnesium sulphate per litre. 1 part of the crystallised dried arsenate dissolved in 31483, and 1 part of the anhydrous salt in 32827 parts of the mixture.

*Solubility in sodium arsenate* (2 parts of the salt in 100 of water).—1 part of the dried arsenate dissolved in 4386, and 1 part of the anhydrous salt in 4604 parts of the solution of sodium arsenate.

*Solubility in a 2 p. c. solution of ammonium nitrate*, rendered slightly ammoniacal.—1 part of the arsenate dried at 100° required 4184, and 1 part of the anhydrous salt, 4389 parts of the nitrate solution.

*Solubility in a 1·5 p. c. solution of potassium chloride.*—1 part of the dried arsenate dissolved in 2440, and 1 part of the anhydrous salt in 2661 parts of the solution of potassium chloride.

*Solubility in a solution of ammonium tartrate* (prepared by dissolving 3·5 grams of tartaric acid in weak ammonia, to slight alkaline reaction, and diluting to 250 c.c.).—1 part of the dried arsenate dissolved in 1410, and 1 part of the anhydrous salt in 1422 parts of the tartrate solution.

*Solubility in ammonium citrate* (prepared by dissolving 2·5 grams of citric acid in ammonia, to weak alkaline reaction, and diluting to 250 c.c.).—1 part of the arsenate dried at 100° dissolved in 889 parts, and 1 part of the anhydrous salt in 933 parts of the citrate solution.

It appears then that ammonio-magnesium arsenate is somewhat soluble in dilute ammonia, but that an excess of magnesia mixture renders the separation of the precipitate more complete.

With regard to the drying of the precipitated ammonio-magnesium arsenate, Puller finds that when dried for a considerable time over sulphuric acid, it contains 6 mol. water, as found by H. Rose; that after drying over the water-bath, or in an air-bath at 100°–102°, it contains exactly  $2(NH_4)MgAsO_4 + H_2O$ ; but that between 103° and 110° it gives off a portion of this water, and a considerably greater portion when dried at 130°.

To avoid the tedious operation of drying the ammonio-magnesium arsenate, it has been repeatedly proposed by Wittstein and others to ignite, as is done with the corresponding phosphate, and weigh as pyro-arsenate. On igniting portions of the salt dried at 100°, (1) over a small gas jet, (2) over a powerful gas flame, and (3) over the blowpipe, it was found that they lost respectively 3·4 p. c., 4·6 p. c., and 8 p. c. When, however, the salt was ignited, according to Wittstein's method, by first drying at 130° for two hours, then heating cautiously on a sand-bath, heating over a Bunsen burner for another two hours, then on an iron plate for an hour and a half, then for twenty minutes over the bare flame, and lastly, by heating intensely over the blowpipe flame, satisfactory results were obtained. On applying the same operation to the salt dried over sulphuric acid, equally good results were obtained. Filters containing small quantities of the arsenate, when soaked with a solution of ammonium nitrate and then deflagrated, showed but a trifling loss. When the dried salt was heated in a current of oxygen, according to Rose's directions—gently at first, then over a Bunsen burner for a quarter of an hour, and finally very intensely over the blowpipe lamp—good results were obtained, and Puller prefers this method to the extremely tedious method of drying at 100° till the weight becomes constant.

On repeating H. Rose's experiments of reducing ammonio-magnesium arsenate to arsenic with formation of arsenious sulphide (by mixing with powdered or freshly precipitated sulphur and heating in a current of hydrogen gas, Rose's observation that the arsenic cannot be removed entirely in this manner was confirmed.

By heating the arsenate with acid ammonium sulphite, the arsenic acid is completely reduced to arsenic which volatilises. The results obtained by weighing the residuary magnesium sulphate are, however, a little too high, on account of the action of the acid sulphate upon the crucible.

Experiments were also made to determine whether, as is known to be the case with the precipitated ammonio-magnesium phosphate, any basic magnesium sulphate or magnesia is ever carried down by the ammonio-magnesium arsenate, and whether

dissolving in hydrochloric acid and reprecipitation with ammonia eliminates any slight admixture of magnesium compounds. Traces of a sulphate and likewise slight traces of arsenic, as indicated by barium chloride and by sulphuretted hydrogen, were invariably found. By precipitating a standard solution of sodium arsenate with varying quantities of the mixture of sal-ammoniac and magnesia salt, it was found that a trifling quantity only of magnesium hydrate or basic magnesium sulphate is precipitated with the arsenate; that especially, a concentrated solution of sal-ammoniac interferes with the precipitation by holding a little of the ammonio-magnesium arsenate in solution, whereas a small excess of magnesia mixture ensures complete precipitation; lastly, that the errors arising from the precipitation of a little basic magnesium sulphate, and from the solubility of the ammonio-magnesium arsenate, nearly neutralise each other, unless an excessive amount of magnesia mixture and sal-ammoniac is employed. Puller proposes to allow for every 16 c. c. of the filtrate '001 gram of arsenate, and recommends precipitating only once, on account of the solubility of the arsenate in sal-ammoniac.

He arrives at the conclusion that the determination as magnesium pyro-arsenate according to Wittstein, when carefully executed, is as accurate as could well be desired, and far more expeditious than drying at  $100^{\circ}$ . For like reasons, he recommends the use of red fuming nitric acid, in preference to all other methods of oxidation (especially after removing the greater part of the precipitated arsenious sulphide mechanically from the filter-paper, and extracting the last traces with ammonia), in order to convert the trisulphide into arsenic acid. The excess of acid is evaporated, and the residue dissolved in a little hydrochloric acid.

### 3. Determination as Uranic Pyro-arsenate, $2(\text{UO}_2)^+ \cdot \text{As}_2\text{O}_7$ .

On adding uranic acetate to a solution of an arsenate in water or in acetic acid, a precipitate of uranic arsenate  $(\text{UO}_2)^+ \cdot \text{HAsO}_4^- + 4\text{H}_2\text{O}$ , is obtained, which loses its water at  $123^{\circ}$ . In presence of ammonium salts a glutinous yellowish green precipitate of ammonio-uranic arsenate  $(\text{UO}_2)^+ \cdot \text{NH}_4^+ \cdot \text{AsO}_4^- + \text{aq}$  is left, insoluble in water and acetic acid, but soluble in mineral acids. On ignition, light yellow uranic pyro-arsenate  $2(\text{UO}_2)^+ \cdot \text{As}_2\text{O}_7$  is obtained. The precipitation is assisted by boiling, and the precipitate subsides more readily on adding a few drops of chloroform to the warm solution, and then boiling up again. The quantitative results being, however, unsatisfactory, Puller found that, on ignition, a small portion of the salt is reduced by the escaping ammonia gas. This source of error was to a great extent eliminated by igniting, as in the case of the corresponding magnesium arsenate, with great care, heating first over a sand-bath, then on a hot iron plate, and lastly over the bare flame, or by igniting at once in a current of oxygen.

Excess of ammonia or sal-ammoniac exerted no disturbing influence. Conversion of freshly precipitated arsenious sulphide into arsenic acid by means of potassium chlorate and hydrochloric acid, or by treating with fuming nitric acid and subsequent precipitation in an acetic solution as ammonio-uranic arsenate, gave very good results; and since the precipitate could be readily washed out—a desideratum of no small importance—this method of determining arsenic is strongly recommended as preferable to all other methods.

**Volumetric Estimation** (Waits, *Zeitschr. anal. Chem.* x. 158). The methods generally used for estimating arsenious acid volumetrically are: 1. by means of free iodine; 2. by means of potassium dichromate; 3. by means of potassium permanganate.

The iodine method depends upon the conversion of arsenious into arsenic acid in alkaline solution; in an acid solution arsenious acid can exist in presence of iodine or chlorine, and is only partly converted into the higher oxide. The alkali must be in the form of a carbonate, for a caustic alkali combines with the iodine.

Normal sodium carbonate fixes iodine, but the acid carbonate does not; a solution saturated in the cold should be used. In employing a standard solution of arsenious acid in hydrochloric acid, the free acid must be neutralised with caustic soda or acid sodium carbonate. With an excess of this latter salt, good results are obtained.

Experiments made with the view of converting precipitated arsenious sulphide into arsenious acid by the action of an ammoniacal solution of silver nitrate upon the sulphide dissolved in ammonia, as well as by means of freshly precipitated bismuthous hydrate, and of substituting in this the trisulphide—which can be obtained in a state of great purity—for the trioxide, were unsuccessful, as the reaction is never quite complete, owing to the formation of sulpho-salts of silver and bismuth.

The method first proposed by Kessler (*Zeitschr. anal. Chem.* x. 205) of determining arsenious acid in an acid solution by means of potassium dichromate, and standardising back by means of a ferrous sulphate solution, gave good results. Excess of hydro-

chloric acid must be avoided. Kessler succeeded in oxidising arsenious sulphide by treating it in a hydrochloric acid solution with mercuric chloride, a saturated solution of which converts the sulphide, slowly at the ordinary temperature, more rapidly on the application of a gentle heat, into the trioxide. The reaction is over when the mass has become white. The experiments of Waitz show further, that the mixture of trisulphide and sulphur which is obtained when a solution of arsenic acid is precipitated with sulphuretted hydrogen, cannot be converted directly into arsenious acid by digestion with mercuric chloride, on account of the dense nature of the precipitate, but that it is readily acted upon, after dissolving out the trisulphide by means of dilute ammonia, and reprecipitating with hydrochloric acid.

The oxidation of arsenious into arsenic acid by means of potassium permanganate is not perfect (*Zeitschr. anal. Chem.* x. 158), and a volumetric method based upon this reaction was found to be most untrustworthy; but, by adding excess of permanganate, more than double the amount required according to theory, and standardising back with a solution of ferrous sulphate, very accurate results were obtained.

The volumetric determination of arsenic acid by means of uranic acetate in presence of free acetic acid and an alkaline acetate was not found to yield trustworthy results.

On the Separation of Arsenic from tin, see TIN.

**Arsenic and Arsenious Acids and Oxides.** *Crystalline Form of Arsenious Oxide.*—Crystals of this body from the Halsbrück Works, near Freiberg, have been examined by P. Groth (*Pogg. Ann.* cxxxvii. 414). They are rhombic prisms, having a broadly tabular form from predominance of the faces which truncate the acute edges. The axial ratio is  $a : b : c = 0.3758 : 1 : 0.3500$ , which is sufficiently near to that of rhombic antimonious oxide (antimony-bloom), viz.  $0.3869 : 1 : 0.3710$ , to show that these two similarly constituted bodies are isomorphous. In their optical properties the two oxides differ considerably. Their specific gravities in both forms are as follows:—

		As <sup>2</sup> O <sup>3</sup>	Sb <sup>2</sup> O <sup>3</sup>
Regular	. . . .	3.70	5.26
Rhombic	. . . .	4.25	5.57

*Reaction of Arsenic Acid with Hydrochloric Acid.*—Rosco (*Pogg. Ann.* cv. 573) found that a concentrated aqueous solution of arsenic acid distilled with fuming hydrochloric acid yielded a distillate free from arsenic, no volatile chloride of arsenic being formed. According to Mayerhofer, however (*Ann. Ch. Pharm.* clviii. 326), the distillate thus obtained always contains arsenic, hydrochloric acid of sp. gr. 1.1 yielding traces, and fuming hydrochloric and considerable quantities of arsenic in the distillate. This result depends upon the reducing action of hydrochloric acid on arsenic acid, whereby arsenious acid and chlorine are produced, the arsenious acid being thus converted by the excess of hydrochloric acid into arsenious chloride, which distils over. Arsenic anhydride reacts with hydrochloric acid gas, even in the cold, forming chlorine-water and arsenious chloride:—



It follows from these results that hydrochloric acid cannot be freed from arsenic by heating it with chlorine or with manganese dioxide, to convert arsenious into arsenic acid, and then distilling. The purification may however be effected by Bettendorff's method with stannous chloride (*1st Suppl.* 216), or by diluting it with water, and submitting it to prolonged treatment with hydrogen sulphide.

*Preparation of Crystallised Arsenates.*—W. Skoy (*Chem. News*, xxii. 61) has obtained the arsenates of calcium and zinc in the crystalline form by mixing the solution of a calcium or a zinc salt with a soluble arsenate, in such proportion that the liquid shall remain acid, and the precipitation shall take place slowly. Similar and more complete results have previously been obtained by Debray and by Lechartier (*1st Suppl.* 222).

When arsenious acid or an arsenite is treated with sodium-amalgam, a substance is produced which reduces potassium permanganate and the salts of gold, silver, mercury, and copper at ordinary temperatures. The colourless aqueous solution decomposes gradually, turning brown and giving off arsenetted hydrogen (Frémy, *Compt. rend.* lxx. 61).

Arsenious oxide is attacked by phosphorus trichloride at 110°, becoming brown from separation of arsenic. On raising the heat to 180° to ensure the completion of the reaction, the liquid, which is very much diminished in quantity, exhibits the characters of arsenious chloride, AsCl<sub>3</sub>, boiling at 132°. The separated



solid bodies consist of metallic arsenic and phosphoric oxide. The reaction may therefore be represented by the equation:—



Arsenic oxide,  $\text{As}^2\text{O}^3$ , is not acted on by phosphorus trichloride, even at  $200^\circ$  (Michaelis, *Jenaische Zeitschr.* vi. 239).

*Separation of Arsenious and Arsenic Acids.*—The mixture is distilled with sulphuric acid and sodium chloride, whereby the arsenious acid is converted into arsenious chloride, which distils over, while the arsenic acid, being unacted on, remains in the retort. The distillate is treated with hydrogen sulphide. The arsenic acid in the residue of the distillation is reduced to arsenious acid by sulphurous acid; the arsenic then precipitated by hydrogen sulphide; the precipitate dissolved by hydrochloric acid and potassium chlorate; and the arsenic acid thereby produced is precipitated as ammonio-magnesian sulphate. This gives the quantity of arsenic acid originally present. The sulphide precipitated from the distillate is treated in the same manner, and thus the quantity of arsenious acid is determined. This method may be applied to the estimation of arsenic in commercial fuchsine, in which both the acids of arsenic are generally present (Riecker, *Zeitschr. anal. Chem.* ix. 516).

*Arsenic Ethers.* (Crafts, *J. Pharm.* [4] xiii. 250). *Ethyl Arsenate* has been already described (1st Suppl. 226).

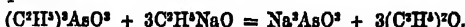
*Methyl Arsenate*,  $(\text{CH}^3)^3\text{AsO}^4$ , is prepared by the action of methyl iodide on silver arsenate. It cannot be distilled without decomposition at atmospheric pressure; the greater part, however, distils undecomposed at  $213^\circ$ – $215^\circ$ . Under the pressure of 60 mm. it distils at  $128^\circ$ – $130^\circ$ . Its specific gravity at  $14.5^\circ$  is 1.5591, that of water at  $4^\circ$  being 1. It resembles the ethyl-compound in all its properties.

*Amyl Arsenate* is prepared in the same manner as the preceding compound, but it has not been obtained quite pure, on account of its partial decomposition at the boiling point, even in a vacuum. It undergoes decomposition with water as easily as the other ethers of arsenic acid.

*Arsenious Ethers.* The properties of *ethyl arsenite* have also been described (1st Suppl. 221). The best mode of preparing it is by the action of sodium ethylate on arsenious chloride or bromide in alcoholic solution:



This mode of preparation is complicated by a secondary reaction, which becomes considerable when a certain proportion of ethyl arsenite is formed in the liquid. Sodium alcoholate, in fact, acts as readily upon ethyl arsenite as upon arsenious bromide, according to the equation:



For this reason a quantity of sodium ethylate is employed, sufficient to react with three-fourths only of the arsenious bromide, so that at the end of the operation there remains a mixture of the bromide and ethyl arsenite. These liquids are separated by passing into the solution a current of dry gaseous ammonia, which forms with the arsenious bromide a compound insoluble in alcohol and ether, whilst it does not affect the ethyl arsenite. The liquid is then filtered, and the ethyl-compound is obtained pure by distilling off the alcohol or ether with which it is mixed.

Ethyl arsenite is not acted on by dry ammonia, and may even be distilled in the gas without alteration. It undergoes with hydrobromic acid a decomposition the reverse of that which usually takes place between haloid acids and ethers, thus:



*Methyl Arsenite*,  $(\text{CH}^3)^3\text{AsO}^3$ , is formed under the same conditions as the ethyl-compound. It boils without decomposition at  $128^\circ$ – $129^\circ$ . Its density is 1.428, that of water at  $4^\circ$  being 1. The density of its vapour at  $197^\circ$  is 6.006. In its other properties it exactly resembles ethyl arsenite.

*Amyl Arsenite*,  $(\text{C}^4\text{H}^{11})^3\text{AsO}^3$ , obtained by the action of sodium amylate on arsenious bromide, distills under the ordinary pressure at  $288^\circ$ , with partial decomposition, and under the pressure of 60 mm. at  $193^\circ$ – $194^\circ$ , without decomposition; it resembles the corresponding ethyl- and methyl-compounds, and is easily decomposed by water, the moisture of the atmosphere, or aqueous alcohol.

The differences in boiling point due to the substitution of methyl for ethyl in these ethers are not so great as those which are observed in most ethers of organic acids; the differences for the ethers of arsenic acid are not the same as for those of arsenious acid. (Crafts.)

**Arsenic Phosphide,  $Pa_s$ ,** is produced, with evolution of hydrogen chloride, when dry arsenetted hydrogen is passed over phosphorus trichloride, or phosphoretted hydrogen over arsenic trichloride. It has a bright roddish-brown colour when first deposited, but becomes dark and lustreless when dry. It is insoluble in alcohol, ether, and chloroform, but dissolves slightly in carbon sulphide. Sulphuric and hydrochloric acid have no action on it in the cold, but appear to dissolve it partially when heated. Strong nitric acid oxidises it, with production of flame, and the same acid, when dilute and warm, oxidises it readily to arsenic acid and phosphoric acid. Potash-solution, ammonia, and baryta-water decompose it slowly in the cold, and more rapidly on the application of heat, phosphoretted hydrogen, arsenetted hydrogen, phosphorous acid, arsenious acid, and metallic arsenic being produced. After long heating, the solution contains phosphoric acid and very little arsenious acid, the greater portion of the arsenic having separated in the metallic state. When arsenic phosphide is heated, it burns to arsenious oxide and phosphoric oxide, and when heated in a closed vessel it is decomposed, the phosphorus subliming before the arsenic. When arsenic phosphide is treated with water, a substance having the composition  $As^{10}P^{20}O^{18}$  is obtained. This substance is not much acted on by acids, with the exception of nitric acid. With alkalis it reacts like arsenic phosphide, but a considerable quantity of arsenic is set free even in the cold. It is decomposed slowly when heated to  $100^{\circ}$ , and rapidly at  $250^{\circ}$  (Janowsky, *Deut. Chem. Ges. Ber.* vi. 216).

Pellotier described a phosphide of arsenic produced by melting phosphorus and arsenic together under water; but, according to Janowsky, the product thus formed is not a definite compound, since it yields up its phosphorus to carbon sulphide.

**Sulphides of Arsenic.** These compounds have recently been examined by Nilsson (*Deut. Chem. Ges. Ber.* iv. 989), who has come to the conclusion that arsenic forms only three definite sulphides, viz.,  $As^4S^3$ ,  $As^3S^2$  and  $As^2S^3$ , the black sulphide  $As^{10}S^8$  described by Berzelius, and the higher sulphides,  $As^4S^{10}$  and  $As^2S^{12}$ , being merely mixtures.

1. The *bisulphide*,  $As^2S^2$ , does not possess the power of forming salts, as stated by Berzelius.

2. *Trisulphide or Arsenious Sulphide*,  $As^2S^3$ .—Alkaline sulphhydrates, saturated under ordinary circumstances with the trisulphide, yield, for the most part, brown amorphous compounds having the general formula,  $R^2S.As^2S^3 + x$  aq. Strontium alone yields a bibasic salt. In a vacuum, on the other hand, larger quantities of hydrogen sulphide are driven off, and well crystallised salts of a more basic character are often obtained, the sulphides of barium and strontium yielding the salts,  $2R^2S.As^2S^3$  and  $3R^2S.As^2S^3$ , and calcium sulphide forming the salt  $7CaS.As^2S^3 + 25$  aq.—In the case of the true alkaline sulphhydrates, the increased elimination of hydrogen sulphide is accompanied by a totally different reaction. With the sulphhydrates of potassium and sodium, metallic arsenic is separated, and a salt of arsenic sulphide,  $3R^2S.As^2S^3 + x$  aq., is formed. Ammonium sulphhydrate,  $(NH^4)^2S.H^2S$ , forms with arsenious sulphide, under all circumstances, the salt  $(NH^4)^2S.3As^2S^3$ ; rarefaction of the air merely causes the escape of ammonium sulphide, together with the hydrogen sulphide.

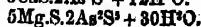
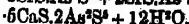
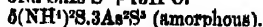
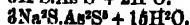
Similar acid salts are produced by treating the monobasic salts with water, thus  $K^2S.As^2S^3 + 5$  aq., gives at first  $K^2S.2As^2S^3$ , and after prolonged boiling with water, the triacid salt,  $K^2S.3As^2S^3$ . When the calcium salt,  $CaS.As^2S^3 + 10$  aq., is treated with cold water, the brown salt,  $CaS.4As^2S^3 + 10$  aq., remains behind, while warm water leaves the yellow salt,  $CaS.9As^2S^3$ .

The triacid sulpharsenites of potassium and sodium are also formed, when a boiling solution of the corresponding carbonate is mixed to saturation with arsenious sulphide. The bisulphide  $As^2S^3$  is then also formed, together with well crystallised oxysulpharsenates, namely, with potassium, the previously known salt,  $K^2O.As^2S^3O^3 + 2$  aq.; with sodium the salt  $Na^2O.2As^2S^3O^3 + 7$  aq.

The saturating capacity of arsenious sulphide appears therefore to be capable of wide variation, inasmuch as salts exist containing 1, 2, 3, 4, 6, and 9 mols. of  $As^2S^3$  to 1 mol.  $R^2S$ , besides basic salts with 2, 3, 7  $R^2S$  to  $1As^2S^3$ , or  $3R^2S$  to  $2As^2S^3$ .

3. *Pentasilphide or Arsenic Sulphide*,  $As^2S^5$ .—The precipitate thrown down by hydrochloric acid from a dilute solution of sodium sulpharsenate, is a sulphhydrate,  $3H^2S.As^2S^5$ , which gives up the whole of its hydrogen sulphide only after prolonged boiling.

By dissolving the pentasilphide in alkaline sulphhydrates, the following salts are obtained:—



Most of these salts are  $\frac{1}{2}$ -basic, and in some of them the pentasulphide of arsenic is partly reduced to trisulphide.

Gélie (*Compt. rend.* lxxvi. 1205) also finds that the compounds of sulphur and arsenic are not so numerous as was formerly supposed. Sulphur heated with excess of arsenic forms only one product, viz., the bisulphide, which is opaque, has a coral-red colour and a crystalline fracture. When the sulphur is in excess, a mixture is obtained consisting of the pentasulphide and free sulphur, from which the former may be dissolved out by ammonia. If the mixture be distilled in an earthenware retort, sulphur goes over first, then a mixture of sulphur and arsenic, and the residue in the retort consists of arsenic pentasulphide. If the distillation be continued, the pentasulphide decomposes into sulphur and arsenic trisulphide, and the latter may be distilled without decomposition.

The mixture of sulphur and arsenic which distils over after the sulphur, when treated several times with carbon sulphide, yields a product containing from 9.27 to 11.41 atoms of sulphur to one of arsenic. As these numbers agree nearly with the formula  $\text{As}_2\text{S}^{10}$ , Gélie suggests that the compound thus obtained may be regarded as an arsenic pentasulphide containing five pairs of sulphur-atoms united into bivalent groups:  $\text{As}_2(\text{S}-\text{S})^5$ .

When sulphur and arsenic are heated together in proportions within the limits indicated by their two extreme compounds,  $\text{As}_2\text{S}^4$  and  $\text{As}_2\text{S}^{10}$ , mixtures of di-, tri-, and pentasulphide are obtained according to the quantity of each used; the trisulphide being either formed directly or from the decomposition of the pentasulphide.

**ARSENIC-GLANCE.** This name has been given to two minerals from the Palm-tree mine at Marionberg, in Saxony: one of which, distinguished by brilliant metallic lustre and perfect monotomic cleavage, was found by Korsten to contain 97 p. c. arsenic and 3 p. c. bismuth; while the other, which occurs in irregular plates and nodules, appears to be merely impure metallic arsenic, its analysis giving:

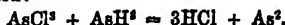
As.	Sb.	Fe.	Ni.	S.
92.80	2.28	1.60	0.26	1.06 = 98.00.

Both varieties when set on fire continue to burn with a glimmering light. This property was shown by v. Kobell to belong to all varieties of finely divided arsenic, whence he inferred that arsenic-glance is not a distinct mineral species. It is most probable, however, that the first-mentioned mineral is really a distinct species, as its specific gravity, 5.3, is lower than that of either of its constituents, viz., arsenic 5.7 and bismuth 9.7 (*Fronzel, Jahrb. f. Mineralogie*, 1873, 25).

**ARSINES.** Pure arsine or arsenetted hydrogen,  $\text{AsH}_3$ , is best obtained by the action of dilute acids on sodium arsenide, prepared by heating sodium in the impure gas evolved when arsenical zinc is treated with dilute acid.

When dry arsine is passed over *phosphorous chloride* kept cool, hydrogen chloride is evolved, and a phosphide of arsenic,  $\text{AsP}$ , is deposited.

When arsine is passed into *arsenious chloride*, hydrogen chloride is evolved, and metallic arsenic is deposited:



When arsine comes in contact with concentrated sulphuric acid, hydrochloric acid, or moist hydrochloric acid gas, metallic arsenic is deposited, and this deposited arsenic dissolves in sulphuric acid on the application of heat, sulphurous acid being evolved (*Janowsky, Deut. Chem. Ges. Ber.* vi. 216).

*Compounds of Triethylarsine with Platinous Chloride.*—When triethylarsine is added by drops and with agitation to a concentrated aqueous solution of *platinic chloride* mixed with an equal volume of alcohol, great heat is evolved, the solution becomes lighter in colour, and ultimately brownish-yellow, and on cooling deposits sulphur-yellow crystals, consisting of a mixture of two isomeric bodies,  $2\text{As}(\text{C}_2\text{H}_5)_3 \cdot \text{PtCl}_4$ , one soluble, the other insoluble in ether. Their formation is represented by the equation:



The soluble salt separates from the ethereal solution by spontaneous evaporation in transparent amber-coloured crystals, isomorphous with the corresponding phosphine-compound. From boiling alcohol it crystallises in more slender, opaque, sulphur-yellow prisms. The isomeric salt, insoluble in ether, dissolves easily in boiling alcohol, and crystallises therefrom, on cooling, in long prisms of a faint yellow colour. When a solution of either of these salts in absolute alcohol is treated with an alcoholic solution of *bromide, iodide, sulphhydrate, or acetate of potassium*, chloride of potassium separates out, and the solution when evaporated yields well crystallised

compounds, having the composition of the salts above described, with bromine, iodine, &c. substituted for the chlorine. Both the isomeric chlorine salts unite with triethylarsine, forming the compound  $4\text{As}(\text{C}^2\text{H}_5)_3 \cdot \text{PtCl}_2$ , analogous to tetrammonio-platinous chloride (Cahours a. Gal, *Compt. rend.* lxxi, 208).

**Palladium-Compound.**—Palladic chloride reacts with triethylarsine in the same manner as platonic chloride, forming the compound  $2\text{As}(\text{C}^2\text{H}_5)_3 \cdot \text{PdCl}_2$ , which crystallises in large transparent reddish-yellow prisms, isomorphous with the corresponding phosphine compound (Cahours a. Gal).

**Gold Compound.**—An alcoholic solution of auric chloride, to which triethylarsine is added drop by drop, becomes heated and decolorised: it is necessary, however, to cool the solution, as otherwise metallic gold will be separated. The colourless filtrate yields by spontaneous evaporation splendid long colourless prisms of the salt,  $\text{As}(\text{C}^2\text{H}_5)_3 \cdot \text{AuCl}$ , isomorphous with the corresponding phosphine compound (Cahours a. Gal).

**ASBOLAN.** A specimen of this mineral from Saalfeld was found by v. Kobell, (*Münch. Sitzungsber.*, 1870, i. 46) to contain lithia, also 54 p. c.  $\text{Mn}^2\text{O}_3$ , 4CaO, 0.61 CuO,  $13.4\text{H}_2\text{O}$  and  $23\text{Al}_2\text{O}_3$ .

**ASH OF ORGANIC BODIES.** *Incineration with Bismuth Oxide.*—Considerable difficulty is often experienced in effecting conveniently, and without loss, the incineration of animal and vegetable substances, especially when some of the mineral constituents are volatile, or when the ashes so obtained are fusible. Many and various remedies have been devised to overcome these obstacles, such as the addition of spongy platinum, the carbonates of barium and sodium, oxide of iron, &c.; but the utility of these substances is questionable; and further, their use violates one of the principal laws of chemical analysis, which forbids the employment of any reagent which cannot be readily eliminated, or which may possibly already exist as a natural constituent of the substance analysed.

Béchamp (*Compt. rend.* lxxiii. 337) recommends the employment of bismuth oxide, in the form of a standard solution of the nitrate, as a reagent fulfilling all the conditions required. It is sufficiently infusible, furnishes a certain quantity of oxygen, is never met with in organised bodies, and can be easily eliminated by a volatile reagent incapable of acting upon the products of combustion; and, finally, it forms with sulphuric and phosphoric acids, and with chlorine, combinations sufficiently stable to resist the moderate degree of heat at which the incineration takes place. The combustion is made in the following manner:—

The material, in a finely divided state, is impregnated with a known volume of the bismuth solution, carefully dried and burnt. The ash is then treated with nitric acid, or, if there is no objection, with dilute hydrochloric acid, in which, if the operation has been successfully conducted, the whole should dissolve. The cold solution is decomposed with sulphuretted hydrogen, and the bismuth sulphide having been filtered off, the liquid is submitted to analysis. When the ash contains phosphates, it may be exhausted with very dilute nitric acid, in which bismuth phosphate is insoluble.

*Analysis of Plant-Ashes.* Bunsen (*Zeitschr. anal. Chem.* ix. 233) has assimilated the analysis of plant-ashes to that of mineral waters, in so far that, by the introduction of carbonic acid, he obtains a mixture of neutral salts, and analyses the soluble portion separately from the insoluble. By this means it becomes possible to check the analytical results by calculation, since, in a correct analysis the sum total of the bases must be equivalent to that of the acids. The usual method, of comparing the total of the results with the quantity of substance employed, cannot be depended upon as a verification, if caustic compounds are present, as it then becomes impossible to obtain an exact estimation of the water and the carbon.

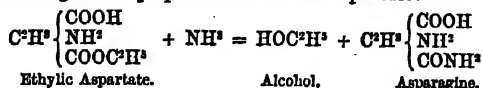
**ASH MANNA.** See MANNA.

**ASPARAGINE.**  $\text{C}^4\text{H}^7\text{N}^2\text{O}_3 = \text{COOH} \cdot \text{CHNH}_2 \cdot \text{CH}_2 \cdot \text{CONH}_2$ . *Formation in Vetches.*—Piria found asparagine in vetches which had been grown exposed to bright light, as well as in those grown in darkness. Some years afterwards Pastour (*Ann. Chim. Phys.* 1857) grew a large quantity of vetches in the garden of the Academy at Strasburg, but did not obtain a trace of asparagine from 200 litres of the sap, whilst he found abundance in vetches grown in the same soil in a cellar. To throw further light on the question, Coessa (*Gazzetta chimica italiana* i. 888) grew some vetches in the month of July, and from a kilogram of those which had been exposed to light, he obtained 16.25 grams of pure asparagine, while from an equal weight of those grown in a cellar he obtained 13.50 grams, the asparagine being proved to be identical in both cases; similar results were obtained in the months of August and September. Pastour's failure probably arose from the circumstances that

the sap of vetches, especially when grown exposed to light, readily ferments, the asparagine being decomposed and ammonium succinate being formed.

*Formation from inactive Aspartic Acid.*—When the silver salt of this acid, prepared from asparagine, is gently heated with ethyl iodide and a little alcohol, monethyllic

aspartate  $C^2H^3 \begin{Bmatrix} COOH \\ NH^2 \\ COOC^2H^3 \end{Bmatrix}$  is obtained as a crystalline substance, which may be dissolved out by ether, and, when heated with strong aqueous ammonia, is converted into asparagine, exhibiting all the properties of the natural product:

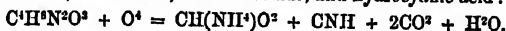


(E. Schaal, *Ann. Oh. Pharm.* clvii. 24).

*Action of Hydrochloric Acid.*—When dry hydrochloric acid gas is passed over asparagine for three days, and the temperature is gradually raised to 180°, a white hard mass is formed. The same product is obtained by boiling asparagine with strong hydrochloric acid and heating the dried mass in a current of carbon dioxide, first to 120° and afterwards to 200°.

The body thus obtained is a mixture of two compounds, both of which are anhydrides of aspartic acid. One, which is sparingly soluble in cold water, can be extracted by boiling water; it has the composition  $C^{16}H^{11}N^4O^3 = 4C^2H^3NO^4 - 7H^2O$ . The residue insoluble in water is  $C^{22}H^{12}N^4O^{11} = 8C^2H^3NO^4 - 15H^2O$ . Both the soluble and the insoluble compound take up water when boiled with ammonia or baryta-water, and are converted into inactive aspartic acid (Schaal).

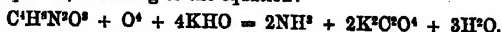
*Action of Potassium Permanganate.*—According to Péan de St. Gilles (*Ann. Chim. Phys.* [3] lv. 394), potassium permanganate does not act upon asparagine even at the boiling heat. According to Campani, on the contrary (*Zeitschr. f. Chem.* [2] vi. 87), the reaction takes place, though slowly, even at ordinary temperatures. When a solution of the permanganate containing 1 gram of the salt in a cubic centimeter is gradually added to a cold saturated aqueous solution of asparagine, the chief products formed are ammonia, formic acid, carbon dioxide, and hydrocyanic acid:



When 1 gram of asparagine and 2 grams of permanganate, both in fine powder, were intimately mixed, and the mixture was poured into 40 c.c. of water and stirred, violent frothing took place, and the temperature rose to 64°; and when a similar experiment was made with 1 gram of asparagine and 4 grams of permanganate, the temperature rose to 94°, and the whole was converted into a brown pasty mass. The final products were, however, the same as those above mentioned. In presence of dilute sulphuric acid (1 gram asparagine, 2 grams sulphuric acid diluted with 30 grams water, and 5 grams permanganate dissolved in the smallest possible quantity of water), the oxidation proceeds in the manner represented by the equation:



in presence of potash, according to the equation:



the oxalic acid not being accompanied either by carbonic or by hydrocyanic acid.

*Estimation of Asparagine.*—R. Sachse (*J. pr. Chem.* [2] vi. 118) describes a method for the estimation of asparagine, depending on the fact that asparagine is converted by prolonged heating with aqueous hydrochloric acid, into ammonia and aspartic acid, and that this acid and asparagine are both unaffected by brominated soda-solution, so that, when the amount of nitrogen liberated on shaking an asparagine solution with the brominated soda-solution, after digestion with hydrochloric acid, is determined by Knop's method (p. 59), the necessary data are obtained for calculating the amount of asparagine present.

The exactness of the method has been tested by a number of experiments with weighed quantities of asparagine (.03–.3 gram) dissolved in 100 c. c. of water, and heated for 12 hours with 10 c. c. of ordinary hydrochloric acid; also with weighed quantities of asparagine mixed with 10 grams of fine pea-flour (which contains no asparagine).

Although an aqueous solution of asparagine may be preserved unchanged, an impure solution containing albuminous substances cannot; it is, therefore, necessary to extract the latter from the vegetable substance in which the amount of asparagine is to be determined, as rapidly as possible. The method adopted by Sachse in the extraction of the asparagine from the mixture with pea-flour, and recommended by

him for general use, is as follows: the 10 grams of flour are heated for 15 minutes with 200 c. c. of a mixture of equal volumes of ordinary alcohol and water in a flask connected with a reversed condenser; the source of heat is then removed; 5 c. c. of a cold saturated solution of mercuric chloride diluted with an equal volume of water added to the hot solution; and the whole, after being well shaken, is filtered through a moderately large fluted filter. The precipitate, which is brought as completely as possible into the filter, is then washed with a second 200 c. c. of heated alcohol and water mixture, afterwards three or four times with cold water. The entire filtrate thus obtained (500–550 c. c.) is evaporated on the water-bath; the residue dissolved as completely as possible in the least possible quantity of water; and the solution and the undissolved matter introduced into a small beaker, and saturated with sulphuretted hydrogen. The precipitate of mercuric sulphide is then removed by filtration and washed with hot water, and the filtrate (100–120 c. c.) is mixed with 10 c. c. of hydrochloric acid and heated to boiling for an hour in a flask attached to a condenser; after cooling, the ammonia is determined by Knop's method. The amount of decomposition which asparagine suffers previous to the treatment with hydrochloric acid, is found to be almost inappreciable. Heating for 1–1.25 hour with the acid is found sufficient to convert the whole of the asparagine into aspartic acid and ammonia; longer heating makes the results too high. It is proposed to employ this method in investigating the formation and movement (*Wanderung*) of asparagine which occurs during the germination of the Leguminosae.

**ASPARTIC ACID.**  $C^4H^7NO_4$ .—This acid is formed from animal proteids by the action of dilute sulphuric acid at the boiling heat; also, together with glutamic acid,  $C^5H^9NO_4$ , by similar treatment of vegetable proteids (1st Suppl. 229, 636).

The relative quantities of these two acids obtained from various vegetable proteids differ very considerably. The proteids of wheat-gluten, gluten-casein, maize-fibrin, and conglutin from lupines and almonds, produce glutamic acid in quantity sufficient to crystallise out of the concentrated mother-liquor on standing for a few days, whereas the quantity of aspartic acid obtained is much smaller. Legumin from pulse, on the contrary, gives but little glutamic acid, but a larger quantity of aspartic acid. The following table gives the roughly estimated quantities by weight of the two acids obtained from various substances:—

	Aspartic acid.	Glutamic acid.
1. Mucedin . . . . .	Not estimated.	25 per cent.
2. Maize-fibrin . . . . .	1.4 per cent.	10.0 "
3. Mixture of vegetable mucedin, and fibrin . . . . .	1.1 "	8.8 "
4. Gluten-casein . . . . .	0.33 "	5.3 "
5. Conglutin (from lupines) . . . . .	2.0 "	3 to 5 "
6. Legumin (from hog-beans) . . . . .	3.5 "	1.5 "

The numbers in experiments 1 to 5 under 'Glutamic acid,' give the quantity which crystallised out of the mother-liquor, and was purified by solution in water. In experiment 6, the glutamic acid adhering to the aspartic acid was also extracted (Ritthausen a. Kreusler, *J. pr. Chem.* [2] iii. 314).

Aspartic acid (from conglutin) crystallises, so long as it is not quite pure, in rather large rhombic prisms, which, according to the measurements of vom Rath, have the axial ratio  $a : b : c = 0.7929 : 1 : 0.5433$ , and are generally combinations of the vertical prism  $\infty P$  with the macrodome  $P\infty$ .

The pure acid can be obtained only in laminae which are not adapted for measurement. The solution of aspartic acid in dilute nitric acid is dextrogyrate:  $[\alpha]_D = + 25.16^\circ$ .

*Cupric aspartate* crystallises in slender blue needles which give off 29.1 p. c. water at  $140^\circ$ , and have the composition  $C^4H^7CuNO_4 + 4\frac{1}{2}H_2O$  (Dessaignes found  $5H_2O$ , see i. 424). The barium and silver salts of the acid obtained as above are similar to those already known. Treated with nitrous acid, they ultimately yield malic acid (Ritthausen, *J. pr. Chem.* cvii. 218).

**ASPIDOLITE.** A rhombic olive-green mica, occurring in oval tabular convex twin-crystals in the chlorite of the Zillerthal. When heated it intumesces, bends, becomes light gray, and acquires a metallic lustre. Hydrochloric acid decomposes it with moderate facility, the silica separating in scales. Hardness = 1.5. Sp. gr. = 2.72:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	MgO	FeO	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O
46.44	10.50	26.30	9.00	4.77	2.52	1.18 = 100.66

(v. Kobell, *J. pr. Chem.* cvii. 167).

**ASTEROÏTE** (Igelström, *Chem. Centrbl.* 1870, 68). A variety of augite, allied

to Jeffersonite, from the magnetic iron of the iron mines of Nordmark in Wermland, Sweden. It forms stellate groups, composed of broad rays, originally ash-grey or white, but acquiring a brown tarnish. It is but slightly attacked by acids, but melts before the blowpipe to a grey non-magnetic slag. The loss of weight by ignition in the following analysis did not occur in other specimens, and appears to have been due to incipient weathering:—

SiO <sup>2</sup>	FeO	MnO	CaO	MgO	Loss by ignition
48.48	22.24	4.12	17.00	4.18	2.83 = 98.85

**ASTRACANTITE.**  $\text{Na}^2\text{SO}^4 \cdot \text{MgSO}^4 + 4\text{H}^2\text{O}$  (Geinitz, *Jahrbuch f. Mineralogie*, 1871, 856; Zincken, *ibid.* 883).—This mineral occurs in the Stassfurt salt-beds, associated with carnallite and kainite. Two specimens (a) of sp. gr. 2.28 and hardness 2-3; (b) of sp. gr. 2.223 and hardness 3.5, gave the following results on analysis:—

	Calculated.	Found.	
		a.	b.
Na <sup>2</sup> O . . .	18.60	18.25	18.50
MgO . . .	12.14	12.64	11.96
2SO <sup>3</sup> . . .	47.79	47.69	47.97
4H <sup>2</sup> O . . .	21.47	21.66	21.44
	100.00	100.24	99.87

**ATACAMITE.** See COPPER OXYCHLORIDES.

**ATELESTITE.** A mineral occurring, together with the bismuth silicate of Schneeberg, in small sulphur-yellow crystals having an adamantine lustre. Of its chemical composition nothing is known, except that it contains bismuth. It is monoclinic, with the axial ratio 0.869 : 1 : 1.822. Angle of inclined axes = 110° 30'. Angle  $\infty P$  :  $\infty P$  = 83° 16', P : P (calc.) = 114° 5½'. Observed forms:  $\infty P$ , P,  $\infty P \infty$ ,  $\frac{1}{2}P \infty$ ,  $\infty R \infty$  (G. vom Rath, *Pogg. Ann.* cxxxvi. 422).

**ATMOSPHERE.** A very extensive series of observations on the impurities existing in the air in various localities has been made by Dr. R. Angus Smith (*Sixth and Seventh Reports of the Inspector under the Alkali Act of 1863*, also *Air and Rain*, London, 1872). Two methods of examination were employed:—1. The examination of the rain-water of the locality; 2. Subjection of the air to artificial washing, and examination of the washings. The latter method is regarded as best adapted for affording an accurate comparison between different atmospheres, since the composition of rain-water necessarily varies according to the amount which falls in a given time, the rain of a dry season being far more impure than the rain of a wet season.

Numerous examinations of rain-water were made, and always by volumetric methods, the smallness of the volume of water at disposal precluding the use of gravimetric methods. The ammonia existing in the free state, or as chloride, sulphate, or carbonate, the albuminoid ammonia derived from the decomposition of organic matter, and the nitric acid, were estimated by Wanklyn, Chapman, and Smith's methods. The hydrochloric and sulphuric acids were determined from the quantity of water required to produce a certain standard amount of whiteness with solution of silver or barium. The permanganate test was applied to the acidified water, the experiments lasting a few minutes only. The more characteristic results are given in the accompanying table (Table I., see next page):—

It appears that the amount of chlorides in rain-water is dependent on the distance from the sea, and on the direction and force of the prevalent winds; the combustion of coal has a slight effect in increasing the quantity. Sulphuric acid is derived chiefly from the combustion of coal, but is also a product of vegetable and animal decomposition; it always increases as we proceed inland. In sea-water the proportion of hydrochloric to sulphuric acid is 100 to 11.6; excess of sulphuric acid over this proportion is due to terrestrial contamination. Free acids are rarely found, save in the rain-waters of towns. Ammonia is chiefly connected with the combustion of coal, and to a lesser degree with the decomposition of organic matter. Albuminoid ammonia is related solely to animal and vegetable life. Nitric acid may be taken as a measure of 'purified sewage.' The permanganate test denotes a variety of products, both from coal and from organic decomposition.

To examine air by washing, 50 c. c. of water are shaken in an empty 2-litre bottle; the washed air then drawn out by one stroke of a flexible bellows-pump having 1½ times the capacity of the bottle; the fresh air which has entered agitated as before, and the operations repeated 10 to 100 times, according to the purity of the atmosphere. In this plan the volume of air used is only known approximately, the results are therefore comparative instead of absolute.

TABLE I.—RAIN WATER: *Average impurities per million parts.*

Where collected.	Hydrochloric acid.	Sulphuric acid (anhyd.)	Sulphuric acid for 100 hydrochloric.	Free acids calculated as sulphuric acid.	Ammonia (inorganic).	Albuminoid ammonia.	Nitric acid.*	Oxygen required as permanganate.
Ireland, Valencia . . . . .	48·67	2·73	6	None	·18	·03	·37	·05
Scotland, five sea coast country places, west . . . . .	12·28	3·61	29	·14	·48	·11	·37	·02
Scotland, eight sea coast country places, east. . . . .	12·91	7·66	59	2·44	·09	·11	·47	·65
Scotland, twelve inland country places . . . . .	3·38	2·06	61	·31	·53	·04	·31	·26
England, twelve inland country places . . . . .	3·99	5·52	138	None	1·07	·11	·75	·47
Scotland, six towns (Glasgow excluded) . . . . .	5·86	16·50	282	3·16	3·82	·21	1·16	1·86
Darmstadt . . . . .	·97	29·17	2998	1·74	—	—	—	—
London† . . . . .	1·25	20·49	1645	3·10	3·45	·21	·84	—
England, six manufacturing towns . . . . .	8·70	34·27	394	8·40	4·99	·21	·85	2·74
Manchester . . . . .	5·83	44·82	788	10·17	5·06	·25	1·01	3·22
Glasgow . . . . .	8·97	70·19	782	15·13	9·10	·30	2·44	10·04

The following table shows the quantities of acids and ammonia contained in air from various localities, compared with the quantities of the same substances (taken as 100) in the purest air from Blackpool, on the Lancashire coast, and at Inellan, on the Firth of Clyde:—

TABLE II.—*Impurities in Air.*

Locality of atmosphere.	Hydrochloric acid.	Sulphuric acid (anhyd.)	Locality of atmosphere.	Ammonia (inorganic).	Albuminoid ammonia.
Blackpool . . . . .	100	100	Inellan . . . . .	100	100
Didbury . . . . .	277	282	London . . . . .	117	109
Buxton . . . . .	415	315	Metropolitan Railway . . . . .	138	271
London . . . . .	320	352	Glasgow . . . . .	160	221
St. Helens . . . . .	516	484	A bedroom . . . . .	194	173
Manchester . . . . .	396	513	Office at Manchester . . . . .	235	193
Metropolitan Railway . . . . .	974	1554	A midden . . . . .	643	301

By means of these air-washings a chemical climatology may be established.

Dr. Smith has also determined the amount of oxygen and carbon dioxide occurring in air under a variety of circumstances; the more characteristic results are as under:

Where collected.	Oxygen per cent.	Carbon dioxide per cent.
Tops of hills, Scotland . . . . .	20·980	·0332
London, parks and open places . . . . .	20·950	·0394
London (average of 68 analyses) . . . . .	20·885	·0439
Glasgow, open places . . . . .	20·929	·0461
Glasgow, closer places . . . . .	20·880	·0539
Metropolitan Railway tunnels . . . . .	20·700	·1452
Theatres, worst parts . . . . .	—	·3200
Mines (average of 339 analyses) . . . . .	—	·7550
When candles go out . . . . .	18·600	—

A series of daily observations on the amount of carbon dioxide in the air has been made at Rostock, by F. Schulze (*Landwirtschaftliche Versuchs-Stationen*, xiv. 886). The following table gives the means for each month during the duration of the

\* Nitrous acid is here included.

† Average of a few specimens only.



experiments, of the parts by volume of carbon dioxide found in 10,000 parts of air:—

1868	1869	1870	1871
October . . 3.0600	January . . 2.7297	January . . 2.9806	January . . 2.9727
November . 2.9040	February . . 2.9214	February . . 2.7621	February . . 3.0135
December . 2.7191	March . . . 3.0487	March . . . 2.8419	March . . . 3.0888
Mean . . . 2.8943	April . . . 3.0973	April . . . 2.8247	April . . . 2.9813
	May . . . . 2.8480	May . . . . 2.8595	May . . . . 3.1191
	June . . . . 2.8960	June . . . . 2.8910	June . . . . 2.9777
	July . . . . 2.8087	July . . . . 2.9368	July . . . . 2.9361
	August . . . 2.8500	August . . . 2.8985	Mean . . 3.0126
	September . 2.8347	September . 2.9720	
	October . . . 2.7964	October . . . 2.9835	
	November . 2.7653	November . 2.9096	
	December . . 2.8008	December . . 2.9976	
	Mean . . . 2.8668	Mean . . . 2.9062	
Total mean, 2.9197.      Maximum quantity, 3.44.      Minimum, 2.25.			

During the latter period of the experiments the carbon dioxide was determined twice in the day by shaking a standard solution of barium hydrate with 4 litres of air, and titrating with oxalic acid, tincture of turmeric being used as an indicator. The results by this method agreed closely with those obtained by passing 25 litres of air through baryta-solution by means of an aspirator.

The lowness of the results may be due to the vicinity of Rostock to the sea, as they most nearly agree with those obtained by Thorpe in the air over the Irish Sea and Atlantic Ocean.

No definite change in the amount of carbon dioxide was observed at different seasons of the year, or at different times of the day. Fog, and also a fall of snow, were often associated with an increase in carbon dioxide. The action of rain is not so obvious; and the changes are probably more dependent on the wind and temperature at the time, and on the action of the moistened soil, whether forming and liberating carbon dioxide or absorbing it. A north-east wind from the Continent was found to increase the carbon dioxide, and a south-west wind to decrease it, probably owing to absorption by the sea. Distilled water shaken up with air was found to dissolve, as a mean, 0.83 milligram of carbon dioxide per litre; fresh fallen rain-water contained 1.073 milligram per litre.

On the detection of organic and other azotised matter in the air, see A. H. Smee (*Chemical News*, xxvi. 25).

*Atmospheric Ozone*.—A very extensive series of observations on the varying amount of ozone in the air has been made by Hönzeu (*Ann. Chim. Phys.* [4] xxvii. 5).

The reagent used consisted of red litmus-paper impregnated over half its surface with a 1 p. c. neutral solution of potassium iodide.

This paper in contact with ozone assumes a blue colour only in the part impregnated with the iodide, this change of colour being due, not to the liberation of iodine, but to oxidation of the potassium, the alkali thus formed changing the colour of the litmus. In this respect the iodized litmus-paper is preferable to iodized starch-paper (Schönbein's reagent), which turns blue when the iodine is set free, and will therefore exhibit this reaction over its entire surface under the influence of free acids, especially nitrous acid, as well as of ozone. The part of the litmus-paper which is not iodized serves to reveal the accidental presence in the air of alkaline vapours (free ammonia, ammonium carbonate, &c.) which turn the red litmus-paper blue throughout its whole length; it is impossible, therefore to mistake the indications. Moreover, the iodized litmus-paper cannot be turned blue by chlorine, bromine, &c., since the chloride and bromide of potassium are neutral.

From a large number of observations made with this reagent in various localities and at different times of the year, the following conclusions are drawn:—

1. The air of the country contains an odoriferous and oxidizing principle which imparts to it a peculiar odour, and the power of blueing iodized red litmus-paper;  
2nd Sup.

also of decolorising blue litmus-paper without previously roddening it; and of destroying certain bad smells.

2. This principle is ozone.

3. Ozone exists in the air normally, but the intensity with which it acts at any given point of the atmosphere is often very variable.

4. The air of the country contains at most about  $\frac{1}{100000}$  of its weight, or  $\frac{1}{700000}$  of its volume of ozone.

5. The manifestation of ozone by the iodised litmus-paper is much more frequent in the country than in town.

6. This difference may be due to the greater circulation of air in the fields.

7. At Rouen, the frequency of the ozone-manifestations varies with the seasons, being greatest in spring, strong in summer, weaker in autumn, and still weaker in winter.

8. The maximum of ozone-manifestation occurs in May and June (16 ozone days per month), and the minimum in December and January (4 ozone days per month).

9. With respect to the frequency of ozone-manifestation, the meteorological year in temperate climates may be divided into two great seasons: the *very active season* (spring and summer), comprising 78 ozone days, and the *feebly active season* (autumn and winter, including 32.

10. In general ozone shows itself more frequently on rainy days (48 ozone days in a hundred of rain, to 28 in a hundred of fine weather).

11. Winds, according to their strength, exert the greatest influence on the manifestation of ozone (24 ozone days in 100 when the air was calm or but slightly agitated, and 60 in 100 when the air was greatly disturbed).

12. At Rouen, the largest number of ozone days occur when the wind is in the west or south-west, the smallest number when it is in the east.

13. Most frequently an exaggerated manifestation of ozone is in intimate relation to the great atmospheric perturbations, known as thunder storms, gales and hurricanes.

14. These great commotions of the atmosphere act at very great distances. Sometimes they momentarily affect the ozone of entire towns and localities, which nevertheless continue to enjoy very fine weather.

15. Atmospheric electricity appears to be the most active cause of the formation of atmospheric ozone.

**ATOMICITY.** A mathematical theory of chemical attraction and atomicity has been proposed by Michaelis (*Deut. Chem. Ges. Ber.* v. 48). The attraction of an atom for other atoms is supposed to be exerted in certain directions only, or rather to exhibit maxima of intensity in these directions, the number of these maxima being in fact the number of units of atomicity exhibited by the atom. The acceleration imparted by any atom to another atom will therefore be a function, not only of the distance between the two, but also of the direction in space of the line joining their centres.

The exact form of the function with regard to the distance is unknown; but it is probably not negative—that is attractive—for all distances, like gravitation, but positive or repulsive for very small distances. Suppose that the force with which the atoms act upon each other varies, like that of gravitation, according to an inverse power of the distance, then the motion of an atom to or from another, regarded as fixed, may be represented by the equation:

$$p = \frac{A}{r^{n+1}} - \frac{A}{r^n}$$

where  $p$  is the acceleration,  $r$  the distance between the atoms,  $n$  and  $m$  any positive whole numbers, and  $A$  a quantity, the value of which is constant for each element (or rather for each pair of elements), but different for different elements. The value of  $p$  is negative or positive according as  $r$  is greater or less than 1. Supposing, then, that for  $r = 1$ , the movable atom has a velocity directed towards the fixed atom; then since for all values less than 1, the acceleration is positive, this velocity will be gradually diminished, as the movable atom approaches the fixed atom, till it is reduced to 0. The repulsion which then ensues carries the atom beyond the point  $r = 1$ , at which the acceleration again changes sign. In this manner an oscillatory movement is imparted to the movable atom, the amplitude of the vibrations being for the most part restricted within certain limits, but capable of becoming infinite for certain values of the velocity, so that the movable atom then no longer returns to the neighbourhood of the fixed atom, or in other words the combination is broken up.

The smaller attractive forces, not in the directions of the maxima, are perhaps concerned in the formation of the so-called molecular combinations.

**ATRACTYLIC ACID**,  $C^{10}H^{14}S^{10}O^{18}$  (Lefranc, *J. Pharm.* [4] ix. 81; x. 325; xvii. 187, 263; *Compt. rend.* lxxvii. 954; lxxvi. 438).—This acid occurs as potassium salt together with inulin, levorotatory sugar, a balsam, and (in May) asparagin, in the root of *Atractylis gummifera*, L., *Carlina gummifera*, Baulin. To prepare it, the dry root is exhausted with water, the solution evaporated, and the residue exhausted with alcohol of 80 p. c. The alcoholic solution, when evaporated, deposits *acid potassium atractylate*,  $C^{10}H^{12}K^2S^{10}O^{18}$ , in short, soft, doubly refracting prismatic needles, which are colourless and scentless, have a bitter taste, are soluble in water and in dilute alcohol, and turn the plane of polarisation to the left ( $\alpha = -5.77^\circ$ ). The dilute solution is not precipitated by barium chloride, but the concentrated solution yields a precipitate of *barium atractylate*, which dissolves in excess of water or on addition of hydrochloric or acetic acid.

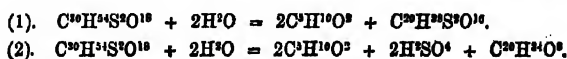
The dry root of *Atractylis* contains 0.5 p. c. of the acid potassium salt, the fresh root 0.1 p. c. This salt may also be directly extracted from the root by alcohol of 75 p. c.; and if the root, after exhaustion with alcohol at  $60^\circ$ , be treated with cold water, it yields the potassium salt of another acid called carlinic acid (*q. v.*).

To prepare *atractylic acid*, the solution of the potassium salt is treated with basic acetate of lead, and the basic atractylate of lead thereby precipitated is decomposed by hydrogen sulphide. The acid is extremely soluble in water; its solution is scentless and colourless, has a very sour astringent, bitter and saccharine taste, and reddens litmus.

Atractylic acid is tribasic; its neutral potassium salt has the composition  $C^{10}H^{12}K^3S^{10}O^{18}$ . It resembles tartaric acid in forming crystalline precipitates with concentrated solutions of the chlorides and sulphates of the alkali-metals; it also forms, with concentrated solution of barium chloride, a crystalline precipitate of acid barium atractylate.

Atractylic acid heated with potassium hydrate above the melting point of the latter is decomposed, with evolution of hydrogen and formation of a resinous body of phenolic character, which is left as potassium salt, together with sulphate, and may be separated therefrom by hydrochloric acid; nitric acid transforms it into a yellow substance resembling picric acid. The formation of this resinous body, which is analogous to that of phenols in general by heating the corresponding sulphonic acids with caustic alkalis, shows that atractylic acid bears a certain resemblance to the acids of which benzene-sulphonic acid is the type; while, in other respects, it is analogous to the sulphuric ethers homologous with sulphovinic acid.

Atractylic acid heated with aqueous potash, baryta, or lime, reacts indeed like the divalentsulphuric ether of a neutral substance,  $C^{10}H^{12}O^8$ , called atractylin. The decomposition, however, takes place by two stages, in the first of which only the elements of valeric acid are separated, the other elements remaining combined in the form of a new acid, also tribasic, called  $\beta$ -atractylic or atractyl-disulphuric acid,  $C^{10}H^{12}S^2O^{18}$ , while in the second stage the molecule is completely resolved into sulphuric acid, valeric acid, and atractylin:



*Beta-atractylic acid*.—When atractylic acid is heated with aqueous potash or baryta, the second stage of the reaction above described follows so quickly upon the first, that it is difficult to obtain the  $\beta$ -atractylic acid; but by the use of lime it is easy to regulate the action and arrest it at the first stage. For this purpose, acid potassium atractylate is dissolved in about 20 parts of water, to which a quantity of slaked lime has been added about equal in weight to the salt; the liquid is gently boiled for 10 or 15 minutes, then filtered, freed from excess of lime by carbonic acid, and evaporated to about a fourth of its original bulk. In this state it is syrupy and uncrystallisable; but on adding a slight excess of hydrochloric acid drop by drop, the whole solidifies to a mass of silky nacreous microscopic needles, consisting of an *acid beta-atractylate of potassium and calcium*, which may be purified by draining on a filter, washing with alcohol and ether, crystallising twice from boiling alcohol of 90 p. c., which dissolves about  $\frac{1}{10}$ th of its weight of the salt, and finally from water.

The conversion of atractylic into  $\beta$ -atractylic acid may also be effected by means of baryta; for, although the passage from the first to the second stage of the reaction is much more rapid in this case than with lime, it is distinctly indicated by the formation of a precipitate of a barium sulphate, so that the reaction can easily be arrested before it has gone too far. Barium atractylate obtained by precipitation from concentrated solutions of the acid potassium salt and barium chloride is boiled

with baryta-water for about a minute, the liquid quickly cooled as soon as it begins to show turbidity, and freed from excess of baryta by a current of carbonic acid gas. The liquid thus neutralised contains valerate and tribasic beta-atractylate of barium. When evaporated to a syrupy consistence, it quickly solidifies to a crystalline mass of well-defined silky needles.

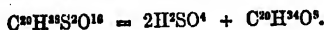
*Tribasic beta-atractylate of barium* differs from the corresponding salt of atractylic acid in its capability of crystallising from water. Its concentrated aqueous solution acidulated with hydrochloric acid solidifies almost immediately to a crystalline mass consisting of an *acid atractylate of barium*,  $C^{30}H^{22}Ba^2S^2O^{12}$ , analogous to the natural acid potassium salt. It crystallises in the same form as the tribasic salt.

The barium-salts of  $\beta$ -atractylic acid are very convenient for preparing the corresponding salts of other metals by double decomposition.

On dissolving the potassio-calcic  $\beta$ -atractylate above described in baryta-water, passing carbonic acid through the liquid to remove the excess of baryta, concentrating the filtrate, diluting it with alcohol till it becomes slightly milky, and leaving it to itself for 24 hours, it solidifies to a mass of very delicate, shining needles, having the aspect and lightness of quinine sulphate and consisting of *potassio-bario-calcic  $\beta$ -atractylate*,  $C^{30}H^{22}Kca^2Ba^2S^2O^{12}$ .\* The composition of this salt confirms the tribasicity of  $\beta$ -atractylic acid.

The  $\beta$ -atractylates resemble the atractylates in most of their reactions, but are distinguished from them by not yielding valeric acid when boiled with alkalis. They are for the most part more soluble both in water and in alcohol than the corresponding atractylates, but crystallise quite as readily.  $\beta$ -atractylic acid further resembles atractylic and also tartaric acid, in forming with the alkali-metals very soluble neutral salts, and acid salts of comparatively sparing solubility.

**ATRACTYLIN**,  $C^{30}H^{24}O^8$  (Lefranc, *loc. cit.*).—This substance is formed as above mentioned by the complete saponification of atractylic acid. To prepare it, however, it is necessary to saponify a beta-atractylate, and not an atractylate, because in the latter case valeric acid is set free as well as atractylin, and these two substances, when thus simultaneously isolated, unite together in such a manner that it is impossible to separate them. The  $\beta$ -atractylic acid, on the other hand, simply splits up, under the influence of alkalis, into sulphuric acid and atractylin:



When potassium  $\beta$ -atractylate is boiled with an equal weight of potassium hydrate dissolved in 30 parts of water, the saponification is complete in less than ten minutes; and if the liquid, which then contains nothing but potassium sulphate and a compound of atractylin with potash, be gradually mixed with a slight excess of hydrochloric acid, the atractylin is set free, together with a varying quantity of atractyligenin (*infra*), resulting from its decomposition, both, however, being retained in solution. To separate them, the liquid is shaken with chloroform, which takes up the atractyligenin, and separates it from the liquid in the form of a white oily soap, while the atractylin remains dissolved, and may be separated by saturating the liquid with common salt. The atractylin then rises to the surface in the form of a flocculent magma, which soon concretes to a solid mass, and may be purified by washing it with ether, and precipitating it several times from a concentrated alcoholic solution by addition of ether.

Atractylin is a white substance having a gummy aspect, no smell, but a strong, peculiar, highly saccharine taste, very soluble in water and alcohol, insoluble in ether and in solution of common salt. It has a slight acid reaction, and unites with alkaline and earthy bases, forming compounds which are very soluble in water, and are gradually decomposed by boiling. Since the atractylates are optically laevogyrate, it is most probable that atractylin possesses the same property; but this point has not yet been verified by experiment.

Atractylin, heated on platinum foil, softens a little above  $100^\circ$ , then swells up and carbonises, giving off white irritating vapours, the odour of which recalls that of frankincense. When cautiously heated in this manner, it leaves a greasy cinder, which burns with a bright flame.

Atractylin dissolves in strong sulphuric acid, with a golden-yellow colour changing to purple-red and then to violet-red under the influence of a slight rise of temperature. This reaction is characteristic of the atractylates and  $\beta$ -atractylates. Nitric acid also dissolves atractylin, without alteration at ordinary temperatures, but on heating slightly, a strong reaction takes place, with production of a yellow substance resembling picric acid (*produit xanthopicroique*).

\*  $ba = \frac{1}{2}Ba$ ;  $ca = \frac{1}{2}Ca$ .

By boiling with very dilute hydrochloric or sulphuric acid, atractylin is partly decomposed in the manner of a glucoside, partly dehydrated. The product of dehydration, called atractyliretin, is a yellowish, non-volatile, insoluble substance, which is likewise produced when the solution of an atractylate or a beta-atractylate is boiled with a strong acid.

The best reagent for effecting the decomposition of atractylin in the manner of a glucoside is solution of caustic potash. Boiled with this liquid, the atractylin splits up into a saccharine substance (different from phloroglucin) and a crystallisable body, atractyligenin, which remains combined with the potash. The formation of atractyligenin in the preparation of atractylin, and the method of separating it by means of chloroform have already been described. It does not appear to have been analysed.

Atractyligenin is a white substance, having a sweetish, somewhat acid taste, nearly insoluble in pure water, but soluble in water containing atractylin, very soluble also in alcohol and in ether, from which it crystallises by spontaneous evaporation in crusts formed of short, brilliant, nacreous needles grouped in stars. Cautiously heated on platinum foil, it melts above  $100^{\circ}$ , to a limpid glass, then sublimates, for the most part unaltered, in white balsamic irritating vapours.

**ATROPINE.** The tri-iodide of this base,  $C^{17}H^{23}NO^3.HI^3$ , is obtained by mixing a solution of the hydriodide with the calculated quantity (2 atoms) of iodine tincture. It forms brown prisms, isomorphous with the corresponding compound of cotarnine. By boiling it with alcohol of 70 p. c., or by precipitating hydrochloride of atropine with periodide of potassium, and crystallising the precipitate from alcohol, the penta-iodide,  $C^{17}H^{23}NO^3.HI^5$ , is obtained in bluish-green laminæ, having a metallic lustre (Jörgenson, *Zeitschr. f. Chem.* v. 673).

The proportion of alkaloids in *Atropa Belladonna* and *Datura Stramonium* has been determined by N. Günthor (*Russ. Zeitschr. Pharm.* viii. 89; *Jahresb.* 1869, 781): for the method adopted, see *Zeitschr. anal. Chem.* viii. 476; *Jahresb.* 1869, 945.

100 parts of the different parts of the plants in the dried state yielded the following quantities of alkaloid:—

<i>Datura Stramonium.</i>					
Seed	Stalks	Leaves	Root		
0.318—0.365	0.063	0.169—0.307	0.065		
<i>Atropa Belladonna.</i>					
Leaves	Stalks	Fruit (ripe)	Fruit (unripe)	Seed	Root
0.833	0.146	0.813	0.955	0.407	0.810

The proportion of atropine in belladonna leaves is smaller in spring than in autumn after the floral organs have faded. 100 grams of dried May leaves yielded 0.392 to 0.421 gram of atropine; the same quantity of dried August leaves yielded from 0.443 to 0.482 gram. No difference is perceptible in the quantity of atropine obtained from wild and from cultivated plants. Roots two to three years old gave 0.472 and 0.489 p. c.; roots seven to eight years old gave only 0.254 to 0.313 p. c. of atropine. Though the root is occasionally richer in atropine than the leaf, it is much more variable in composition; hence the leaf is likely to be more uniform in its therapeutic properties (Lefort, *Pharm. J. Trans.* [3] ii. 1029).

**AUGITE.** Tchermak (*Zeitschr. f. Chem.* v. 634) regards the aluminous augite as isomorphous mixtures of the two silicates,  $CaO.MgO.2SiO^2$ , and  $MgO.Al^2O^3.SiO^2$ ; the aluminous hornblondes as mixture of the three silicates,  $CaO.3MgO.4SiO^2$ ,  $CaO.MgO.2Al^2O^3.2SiO^2$ , and  $Na^2O.Al^2O^3.4SiO^2$ .

**AURIN**,  $C^{20}H^{14}O^3$ .—A red colouring matter produced by heating phenol with oxalic acid and strong sulphuric acid. It was first obtained by Kolbe & Schmitt in 1861, since which time it has been manufactured, and is known in commerce as aurin or yellow corallin. It has been lately examined by Dale & Scherlemmer (*Proc. Lit. Phil. Soc. of Manchester*, vol. xi. No. 2; *Chem. Soc. J.* [2] ix. 468; x. 74), who find that the commercial product is a mixture, from which the pure colouring matter may be extracted by solution in alcohol and treatment with ammonia. A crystalline compound of aurin and ammonia then separates, whilst the other bodies present remain in solution. The ammonia-compound, after being washed with alcohol by means of a filter-pump, is decomposed by dilute acetic or hydrochloric acid, and further purified by repeated crystallisation from strong acetic acid. The specimens thus obtained obstinately retain varying quantities of water and acetic acid, a fact also observed by H. Fresenius (*J. pr. Chem.* [2] iii. 477).

From strong hydrochloric acid, aurin crystallises in fine hair-like red needles, which

when dried at  $110^{\circ}$ , contain a large quantity of hydrochloric acid. For further purification, a dilute alkaline solution was precipitated with dilute hydrochloric acid, and the precipitate washed by the filter-pump, but this product also contained hydrochloric acid, which was only given off above  $110^{\circ}$ . By the spontaneous evaporation of an alcoholic solution, aurin is obtained in dull red crystals with a green lustre, which when dried at  $110^{\circ}$  do not contain any alcohol, but several p. c. of water, which is given off only at a temperature above  $140^{\circ}$ .

From a mixture of alcohol and acetic acid it separates in dark red crystals, moderately thick in comparison with their length. These crystals are trimetric, having the axes  $a : b : c = 0.5604 : 1 : 0.4719$ , and exhibiting the combination 100, 010, 111, or  $\infty P_{\infty} \cdot \infty P_{\infty} \cdot P$ . The face  $\infty P_{\infty}$  has a strong steel-blue reflection. The plane of the optic axes appears to be perpendicular to  $\infty P_{\infty}$  and  $\infty P_{\infty}$ , and therefore parallel to  $OP$ . The red crystals from acetic acid have the same form, but are not so thick in comparison with the length.

Aurin crystallised from acetic acid always retains a portion of that acid, and is therefore unfit for analysis, but by crystallisation from alcohol it is obtained pure and of constant composition. The numbers obtained by analysis agree best with the formula  $C^{21}H^{14}O^3$ , but the mode of formation, as will be explained further on, shows that the formula  $C^{20}H^{14}O^3$ , which also agrees nearly with the analytical results, is more probable.

	Calculated for		Mean of analyses
	$C^{21}H^{14}O^3$	$C^{20}H^{14}O^3$	
C . . .	70.75	70.47	70.73
H . . .	5.06	4.63	5.16
O . . . ,	16.19	15.00	15.11
	100.00	100.00	100.00

The compounds and derivatives of aurin hitherto obtained are not well suited for an exact determination of its molecular weight.

Aurin which has been repeatedly crystallised from acetic acid or alcohol does not melt at  $220^{\circ}$ ; at this temperature the crystals assume a darker shade, which disappears again on cooling, without any appearance of alteration in the substance. When more strongly heated, it melts, emitting at the same time the odour of phenol, and solidifies again on cooling to an amorphous, beetle-green mass. Aurin dissolves readily in alkalis with a magenta-red colour, and is precipitated from this solution by acids as a crystalline powder.

These properties, together with the crystalline form, are sufficient to distinguish aurin from Fresenius's corallin, which melts at  $150^{\circ}$  and crystallises in combinations of prisms and pinacoid planes, whilst aurin does not melt even at  $220^{\circ}$ , and contains only pinacoids and octohedra, which latter are not to be found in corallin; moreover, the axial ratios of the two kinds of crystals, which both belong to the trimetric system, are very different (see CORALLIN).

To compare these two products further, aurin was prepared by heating pure phenol with oxalic acid to  $100^{\circ}$ – $110^{\circ}$  for five or six days, precipitating with water, boiling to remove free phenol and further purifying the resinous product by solution in dilute caustic soda, and reprecipitation with weak hydrochloric acid. A crystalline precipitate was thus obtained, which, when dissolved in alcohol, crystallised out in small but distinct needles, having the colour of chromic trioxide and a diamond lustre, and capable of bearing a heat of  $220^{\circ}$  without alteration. The crystals thus obtained were identical in form with those above described, but the face  $\infty P_{\infty}$  did not exhibit any steel-blue reflection: Aurin prepared from phenol does not retain water like that obtained from the commercial product; but is anhydrous after drying over sulphuric acid, and does not lose weight when heated to  $200^{\circ}$ . The mean results of its analysis were 70.38 p.c. carbon and 5.05 hydrogen, agreeing most nearly with the formula  $C^{20}H^{14}O^3$ .

Aurin from pure phenol is therefore very nearly related to that contained in the commercial product, if not identical with it, and consequently different from Fresenius's corallin. The cause of this difference must be looked for in the different modes of preparation. Fresenius, as well as Kolbe and Schmitt, prepared their compound by heating the mixture to  $140^{\circ}$ – $150^{\circ}$ , whilst the body above described was formed at a temperature not exceeding  $110^{\circ}$ .

The aurin from pure phenol being obtained without the formation of bye-products, the reaction by which it is formed may be expressed by the following equation:—



The phenol used for the preparation of the commercial product always contains a small quantity of cresol; and it appears probable that the latter takes part in the reaction, which might take place as follows:—



This supposition, however, is negatived by the fact that when aurin is carefully heated in a combustion-tube, a reddish, oily liquid distils over, which dissolves almost completely in potash, and when precipitated by hydrochloric acid, dried, and distilled, yields a distillate which boils at  $184^\circ$ , and solidifies on cooling to a mass of crystals consisting of pure phenol, without a trace of cresol, the formation of which might have been expected if it had originally taken part in the production of the aurin. From this, then, it may be inferred that the aurin contained in the commercial product is identical with that obtained from pure phenol, and therefore has the composition  $\text{C}^{20}\text{H}^{14}\text{O}^3$ .

*Compound of Aurin and Sulphur Dioxide* ( $\text{C}^{20}\text{H}^{14}\text{O}^3$ ) $\text{SO}_2$ . When sulphur dioxide is passed into a hot concentrated alcoholic solution of aurin, the dark yellowish-red liquid assumes a lighter colour, and on cooling, a compound of aurin and sulphur dioxide separates out, forming other brick-red crystalline crusts or granular garnet-red crystals having a more or less beetle-green lustre. The compound dried over sulphuric acid does not retain any alcohol, but a considerable quantity of water, which is not expelled at  $100^\circ$ ; but above this temperature it is given off, together with sulphur dioxide. Whether this water is chemically combined or merely adheres to the compound mechanically is not yet decided; if it be in combination, the formula of the hydrated crystals is ( $\text{C}^{20}\text{H}^{14}\text{O}^3$ ) $\text{SO}_2 + 5\frac{1}{2}\text{H}^2\text{O}$ .

*Aurin-potassium Bisulphite*,  $\text{C}^{20}\text{H}^{14}\text{O}^3 \cdot \text{KHSO}_3$ , is produced by adding a solution of potassium bisulphite to a hot, concentrated, alcoholic solution of aurin, until the yellowish-red colour of the latter has disappeared. A soft, white chalky powder then separates, increasing in quantity when the solution is left at rest. Under the microscope it appears to consist of small rectangular plates. It is more soluble in water than in alcohol, and may be recrystallised from hot water; but, on boiling the aqueous solution, decomposition takes place and aurin is precipitated. Acids as well as alkalis decompose it readily, so that it soon acquires a yellow or reddish tint on exposure to the air.

*Aurin-ammonium Bisulphite*, ( $\text{C}^{20}\text{H}^{14}\text{O}^3$ ) $(\text{NH}_4)\text{HSO}_3$ , is obtained by a reaction similar to that which yields the potassium-compound, to which it has the greatest resemblance. The *sodium-compound*  $\text{C}^{20}\text{H}^{14}\text{O}^3 \cdot \text{NaHSO}_3$  is also very much like the two preceding compounds, but appears to be more soluble in water.

**Leucaurin.**  $\text{C}^{20}\text{H}^{16}\text{O}^3$  or  $\text{C}^{21}\text{H}^{18}\text{O}^3$ .—This body is produced by the action of hydrogenising agents on aurin. Kolbe and Schmitt found that their red compound yielded, on treatment with acetic acid and iron filings, a colourless body soluble in alkalis. On exposing this solution to the air, it gradually assumes a red colour, and on adding potassium ferrieyanide, an intensely red liquid is formed at once. The alkaline solution of the red body also becomes colourless in contact with sodium-amalgam, but turns red again on exposure to the air.

Dale and Schorlemmer prepared leucaurin, either by heating an alkaline solution of aurin with zinc-dust and precipitating the colourless liquid with hydrochloric acid, or by acting with zinc-dust on a solution of aurin in acetic acid, or on an acidulated alcoholic solution. On diluting the colourless liquid with water, leucaurin separates as a crystalline precipitate, and from the mother-liquor a further quantity crystallises out in needles on standing.

Pure leucaurin is perfectly colourless; but when recrystallised it readily assumes a yellowish tint. It is freely soluble in acetic acid, crystallising therefrom in thick and tolerably hard prisms, the faces of which are developed at one extremity only, whilst the other extremity is very irregular; it also shows a strong tendency to twin. From an alcoholic solution it was obtained in extremely friable prisms. It may be heated to  $130^\circ$  without melting, assuming, at the same time, a reddish colour; on heating it more strongly, it gradually softens and assumes a deep red colour. Its alkaline solution readily absorbs oxygen, and becomes of a dark red colour on the addition of potassium ferrieyanide. The red compound thus produced is, however, not aurin, but probably an oxidation-product of that body; on adding an acid to the solution, a brown precipitate is formed, which is almost insoluble in alcohol and acetic acid.

The analysis of leucaurin gave, as a mean, 78.84 p.c. C. and 5.93 H., the formula  $\text{C}^{20}\text{H}^{16}\text{O}^3$  requiring 78.94 C. and 5.26 H., and the formula  $\text{C}^{21}\text{H}^{18}\text{O}^3$  79.25 C. and 5.66 H. Leucaurin prepared by heating aurin from pure phenol with acetic acid and zinc-dust gave by analysis (mean) 78.42 C. and 5.70 H., which agrees with the formula  $\text{C}^{20}\text{H}^{16}\text{O}^3$  (78.48 C., 5.83 H.) better than with  $\text{C}^{21}\text{H}^{18}\text{O}^3$  (78.94 C., 5.26 H.); but, as

most of these bodies retain water very obstinately, and to avoid oxidation, the compound was merely dried over sulphuric acid, the formula  $C^{20}H^{18}O^2$  may be regarded as the more probable.

Leucaurin contains three hydroxyls, the hydrogen of which can be easily replaced by acid radicles.

*Triacetyl-leucaurin*,  $C^{30}H^{18}(C^3H^3O)^3O^2$  or  $C^{21}H^{18}(C^3H^3O)^3O^2$ , is formed by heating leucaurin with excess of acetyl chloride, and purified by brisk agitation with cold water, and crystallisation from warm alcohol. It forms short silky needles readily soluble in alcohol and acetic acid, quickly decomposed by boiling water and by alkalis.

*Tribenzoyl-leucaurin*,  $C^{30}H^{18}(C^7H^5O)^3O^2$  or  $C^{21}H^{18}(C^7H^5O)^3O^2$ , is readily formed when leucaurin is heated with benzoyl chloride. It is a very stable body, which is not acted upon by boiling it with weak caustic soda, and may be heated to  $180^\circ$ , and even higher, without decomposition. It is but sparingly soluble in alcohol and acetic acid, but freely in benzene, from which it separates in transparent crystals containing benzene, which they lose when exposed to the air or when heated, the crystals falling to powder.

*Other derivatives of Aurin.* 1. Red Corallin or Pæonin: a colouring matter, which dyes wool and silk with a redder shade than aurin, is prepared by heating aurin with aqueous ammonia to  $140^\circ$ – $150^\circ$ . (See CORALLIN.)

2. Azurin or Azulin is produced by treating aurin with aniline. When aurin is gently boiled with aniline and a little acetic acid, the solution soon assumes a pure blue colour. On boiling the product with dilute hydrochloric acid, in order to remove an excess of aniline, a blue resinous substance is obtained, consisting of a mixture of different bodies, which are partly soluble in alcohol and acetic acid, and partly insoluble therein. By heating the above mixture on a water-bath, a blue solution is formed in 16–20 hours, which, however, also contains several bodies. A portion of the product is readily soluble in caustic soda with a purple colour, and precipitated by acids from this solution in blue flakes, which dissolve in alcohol and acetic acid. The portion which is insoluble in alkalis dissolves completely in acetic acid and alcohol, with a fine blue colour, but ether takes up only a part of it, forming a dark red solution, which on evaporation leaves a blue resinous body. The portion not dissolving in ether forms a dark blue powder with a golden reflection.

#### AZOBENZENE. See BENZENE DERIVATIVES

**AZODIPHENYL BLUE**,  $C^{20}H^{18}N^2$  (Hofmann a. Geyger, *Deut. Chem. Ges. Ber.* v. 472). This blue colouring matter, first obtained by Martius a. Griess (*Ber. Monatsb.* 1865, 640), is produced by the action of azodiphenyldiamine on aniline salts:



its formation being analogous to that of the 'Magdala red' of commerce,  $C^{20}H^{18}N^2$ , by the action of azodinaphthylidiamine,  $C^{20}H^{18}N^2$  on naphthylamine,  $C^{10}H^7N$ .

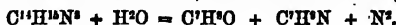
The blue is prepared by heating equal weights of the azo-base and aniline hydrochloride with twice the weight of alcohol to  $160^\circ$  for four or five hours. The product is treated with boiling water, and the residue is dissolved in alcohol with the aid of hydrochloric acid, and reprecipitated by soda. On dissolving the base in alcohol, adding hydrochloric acid, and concentrating the solution, a dark blue crystalline salt is obtained, insoluble in water and in ether, but readily soluble in alcohol, especially when warm. The solution, which is of a deep violet-blue colour, dyes wool and silk. It is decolorised by zinc and hydrochloric acid, but no corresponding leuco-base is thereby produced. Soda precipitates the base from the concentrated alcoholic solution of its salts, as a dark brown powder, which is insoluble in water, but soluble in alcohol or ether; the addition of hydrochloric acid to the latter solution precipitates the base as hydrochloride.

The hydrochloride has the composition,  $C^{20}H^{18}N^2.HCl$ , but loses part of its acid on being dried at a high temperature, or by recrystallisation from alcohol. The hydriodide  $C^{20}H^{18}N^2.HI$  is very similar to the hydrochloride in its properties. The picrate  $C^{20}H^{18}N^2.C^8H^4(NO^2)_3O$  forms a blue powder, quite insoluble either in water or in ether, and only very sparingly soluble in boiling alcohol. This azodiphenyl blue has the same composition as the *violantiline*,  $C^{20}H^{18}N^2$ , obtained by Girard, De Laire, and Chapoteaud (*1st Suppl.* 168), by the oxidation of pure aniline,  $8C^8H^7N - 3H^2 = C^{20}H^{18}N^2$ , but it has not as yet been ascertained whether the two are identical.

Blue colouring matters very similar to the azodiphenyl blue are produced by the action of toluidine or naphthylamine hydrochloride on azodiphenyldiamine. These most likely have the composition,  $C^{20}H^{18}N^2$  and  $C^{20}H^{18}N^2$ , and it is probable that



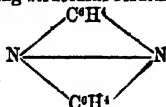
ditolyldiamine would produce similar compounds. All attempts to prepare azo-ditolyldiamine, however, have as yet been unsuccessful. On passing a rapid stream of nitrous acid through fused toluidine floating on a hot saturated solution of common salt, the base gradually solidifies to a crystalline mass, which, when purified by re-crystallisation from alcohol, forms dark yellow needles of *diasoamido-toluene*,  $C^{10}H^{10}N^2$ , the isomeride of azoditolyldiamine; on boiling this with hydrochloric acid, it splits up into cresol and toluidine, with evolution of nitrogen:



The action of this compound on aniline, toluidine, and naphthylamine hydrochlorides produces colouring matters, but the byo-products formed at the same time show that the reaction is very complicated.

**AZOPHENYLENE.**  $C^{12}H^{10}N^2$  (A. Claus, *Deut. Chem. Ges. Ber.* v. 367, 610; vi. 723; *Ann. Ch. Pharm.* clxviii. 1).—This compound is formed by distilling calcium azobenzoate or para-azobenzoate with lime. A red oil then passes over, which solidifies after a while to a crystalline mass consisting mainly of two substances, viz., azophenylene, which forms the principal portion, and a dark red body, the nature of which has not yet been ascertained. On slowly heating this mass in small quantities in a platinum crucible, the azophenylene sublims in light yellow, glistening, slender needles, more than an inch long. It melts at  $170^{\circ}$ – $171^{\circ}$ , and sublims at a higher temperature. It is very slightly soluble in hot water, but may easily be volatilised with aqueous vapour, whereby it is obtained in small almost colourless needles. It dissolves in 50 parts of cold alcohol, easily in hot alcohol, and to some extent in ether and in benzene. With strong nitric acid, it appears to form a nitro-product.

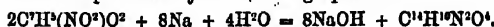
*Constitution of Azophenylene and of Azobenzoic Acid.*—The reactions of azophenylene are best explained by the following structural formula:



In the formation of azophenylene bromide and hydrazophenylene, the bromine- or hydrogen-atoms probably attach themselves to the two nitrogen-atoms, the connection between which is thereby loosened.

But a question then arises as to how this body is derived from azobenzoic acid,  $C^{10}H^{10}N^2O^4$ , which, according to Ströcker, is related to azobenzene in the same manner as benzoic acid to benzene, and therefore ought to yield, by the dry-distillation of its calcium salt, not azophenylene,  $C^{12}H^{10}N^2$ , but azobenzene,  $C^{14}H^{12}N^2$ .

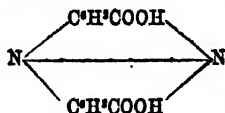
The most probable explanation of the apparent anomaly is, that azobenzoic acid contains 2 atoms of hydrogen less, its true formula being  $C^{10}H^8N^2O^4$ , and this view is supported by the following considerations. If this acid really corresponded with azobenzene, its formation from nitrobenzoic acid by the action of sodium-amalgam (*1st Suppl.* 320) would be represented by the following equation:



But experiment shows that as soon as three-fourths of the quantity of sodium indicated by this equation, that is to say, 6 atoms, have been added, a brisk evolution of hydrogen commences and the reaction is terminated. This shows that it really takes place according to the equation:



Azobenzoic acid is therefore azophenylene-dicarbonic acid,  $C^{10}H^8N^2(COOH)^2$ , or



The calcium salts of meta- and para-azobenzoic acid likewise yield by dry-distillation an azophenylene identical with that which is obtained from ortho-azobenzoic acid.

Azophenylene would probably be formed also by passing azobenzene through a red-hot tube:  $C^{14}H^{12}N^2 - H^2 = C^{12}H^{10}N^2$ .

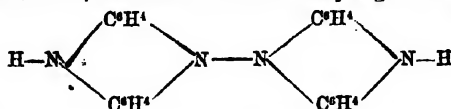
*Azophenylene Bromide*,  $C^{12}H^{10}N^2Br^2$  is formed when bromine is added to a concentrated alcoholic solution of azophenylene, or better when 1 part of azophenylene is

dissolved in 150 parts of benzene and bromine is added as long as yellow needle-shaped crystals continue to separate. These crystals being almost insoluble in benzene containing bromine, the quantity of the bromine-compound obtained by this latter process is very nearly that which is required by calculation.

*Hydrazophenylene*,  $C^6H^4N^2$ , is formed by the action of hydrogen sulphide on an ammoniacal solution of azophenylene in alcohol. Sometimes an intermediate compound, forming deep blue needles, is obtained at the same time.

Hydrazophenylene is almost insoluble in water and benzene, and is taken up by cold alcohol in small quantity only. At about  $200^\circ$  it gives off hydrogen, and is retransformed into azophenylene, the formation of the blue intermediate product being again observable. Boiled with dilute acids, it dissolves and forms salts of a green colour, but not of constant composition. In strong sulphuric acid, it dissolves with dark green colour, changing after a while to yellowish brown; but if the solution be left for some time in contact with moist air, the green colour reappears and masses of olive-green needles separate, which give up sulphuric acid when washed with water, the water at the same time acquiring a green colour. Hydrazophenylene treated with an alcoholic solution of platonic chloride containing free hydrochloric acid yields a platinochloride containing  $2(C^6H^4N^2.HCl).PtCl^4$ , or perhaps  $C^6H^4N^2.2HCl.PtCl^4$ .

On the whole it seems probable that hydrazophenylene does not itself possess the properties of a base, but that a base is formed from it by the action of acids, probably by union of two molecules, with loss of two atoms of hydrogen: thus—



**AZORITE.** On the crystalline form of this mineral, see Struvner (*Jahrbuch f. Mineralogie*, 1871, 751).

**AZULIN** or **AZURIN.** A blue dye, obtained by boiling aurin with aniline (p. 120).

**AZOKULMOKIN.** } See CYANOGEN, ACTION OF AMMONIA ON.  
**AZULMIC ACID.** }

**AZURITE**,  $Cu^2H^2C^2O^6$  or  $3CuO.H^2O.2CO^2$ . Webel a. Tüngel (*Deut. Chem. Ges. Ber.* iv. 188) have examined considerable quantities of the Siberian azurite for ammonia, but with negative results, thereby invalidating the supposition that its deep blue colour is due to a combination with ammonia, as is the case with some other salts of copper, and that it has been formed from malachite in presence of nitrogenous matter. They found, moreover, on heating fragments of marble to  $200^\circ$  in a sealed tube, with solution of cupric sulphate, that the marble became covered with a green carbonate, which, on standing for some months, was converted in many places into a deep blue carbonate, whilst at the same time the whole of the water in the tube disappeared, and numerous crystals of gypsum were deposited. The small quantities of the two carbonates formed, and the difficulty of separating them, have hitherto precluded the possibility of analysing the blue compound quantitatively; its external characters, however, agree so perfectly with those of the natural mineral, that it seems highly probable that azurite has been formed from malachite,  $Cu^2CO^3 + aq.$ , by absorption of carbon dioxide and elimination of water, as in the experiment above described.

## B

**BABINGTONITE.** This mineral from Devonshire has been analysed by D. Forbes (*Phil. Mag.* [4] xxxvii. 328), and from Herbornseelbach in Nassau by John Pogg. (*Ann.* cxliv. 594). The results are given in the following table, together with those of the Arendal mineral, analysed by Rammelsberg (*Mineralchemie*, 477):—

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	MnO	CuO	MgO	Loss by ignition
Arendal . . . .	51.22	—	11.00	10.26	7.91	19.32	9.77	0.44 = 100.92
Devonshire . . .	49.12	1.60	9.78	12.87	1.25	20.87	8.97	0.73 = 99.32
Herbornseelbach .	50.44	—	17.01	7.49	3.22	19.90	1.45	0.43 = 99.54

The composition of the Arendal and Devonshire minerals agrees with Hammelsborg's formula,  $9\text{MO}_2\cdot\text{SiO}_2 + \text{M}^2\text{O}\cdot 3\text{SiO}_2$ , in which the oxygen of the monoxides is to that of the sesquioxides as 3 : 1; in the Nassau mineral this ratio is only 8 : 5; but, in both, the ratio of the oxygen of the silica is to that of all the bases together is 2 : 1.

Babingtonite from Devonshire forms black-green radio-fibrous groups having a sp. gr. of 3·431 to 3·436; hardness = 5·5. It is almost undecomposable by acids, gives off a little hygroscopic water when heated, and afterwards exhibits an alkaline reaction (Forbes). The crystalline form of the Nassau mineral is described by G. vom Rath (*Pogg. Ann. Ergänzungsband*, v. 420).

**BACTERIA.** See FERMENTATION.

**BARIUM.** On the occurrence of barium in silicates, see SILICATES.

*Preparation of Baryta.*—E. Nicklès prepares caustic baryta from heavy spar, by decomposing the mineral mixed with coal or charcoal and sawdust in a furnace of peculiar construction, extracting the resulting barium sulphide with boiling water out of contact with the air, and decomposing it with  $1\frac{1}{2}$  equiv. of zinc oxide. The barium hydrate obtained by evaporating the solution may be converted into anhydrous baryta by heating it in cast-iron or earthen cylinders in the stream of carbonic oxide evolved by the reduction of the sulphate. The sulphide of zinc, when roasted, yields the quantity of oxide required for another operation (*Bull. Soc. Chim.* [2] xii. 494).

A similar process is described by Rosenstiehl (*Dingl. polyt. J.* cxviii. 64; *Jahresb. f. Chem.* 1870, 1122).

*Barium Hydrate.*—According to Rosenstiehl a. Rühlmann (*Chem. Centrbl.* 1870, 684), crystallised barium hydrate melts in its water of crystallisation at  $75^\circ$ , the crystals then contain 45·97 p. c. BaO.

The solubility of baryta in water at different temperatures is given in the following table:—

Temp.	Anhydrous BaO in 100 water	Temp.	Anhydrous BaO in 100 water	Temp.	Anhydrous BaO in 100 water
0°	1·5	22°	3·7	59°	17·5
6	1·8	30	5	64	23·8
6·5	1·9	36	6·4	68·5	27·7
12	2·4	41	7·6	69	31·6
12·5	2·9	46	9·5	70	31·9
16	3	54	14	73	44·9
21	3·6	58·5	17·2	77	70

**BARLEY.** The following observations relating to the life and growth of barley have been made by J. Fittbogen (*Landw. Versuchs-Stationen*, xiii. 81). The plants were reared in pots, and sand purified by ignition, digestion with sulphuric acid, and washing till every trace of acid was removed, was used as an indifferent soil-material. Into glass cylinders were put first a layer of quartz, then of unsized cotton, and lastly the purified sand. 18 barleycorns were sown in each pot, at a depth of 2·5 c.m., having been previously sprouted between two layers of damp filter-paper. The manure for each pot, expressed in milligram-equivalents was:

$\text{KH}_2\text{PO}_4$	KCl	$\text{MgSO}_4$	$\text{Ca}(\text{NO}_3)_2$	$\text{Fe}^{2+}$	$\text{SiO}_2$
2·0	1·0	1·6	16·0	5·0	10·0

Thirty pots were so arranged. Plants were cut twice before the ear appeared, and three times afterwards. There were thus five periods. The plants were merely divided into two parts: that above the surface of the earth, and that beneath it, except in the last two periods, when a separation was made between the straw and the seed.

The aerial organs of 100 plants contained on an average:—

Grams	1st period	2nd period	3rd period	4th period		5th period	
				Grain	Straw and chaff	Grain	Straw and chaff
Organic matter . . . . .	11.821	44.083	106.667	41.250	99.896	74.654	80.308
Ash . . . . .	1.854	3.400	4.576	1.000	3.563	1.388	3.767
Dry substance . . . . .	13.675	47.483	111.234	42.250	103.459	76.042	84.075
Potash . . . . .	0.748	0.951	0.957	0.229	0.459	0.235	0.495
Soda . . . . .	0.045	0.066	0.080	0.000	0.112	0.012	0.104
Lime . . . . .	0.223	0.569	0.924	0.058	0.980	0.087	1.045
Magnesia . . . . .	0.075	0.216	0.282	0.095	0.237	0.149	0.168
Ferric oxide . . . . .	0.021	0.031	0.088	0.022	0.035	0.131	0.137?
Phosphoric acid . . . . .	0.216	0.454	0.601	0.384	0.205	0.566	0.159
Silica . . . . .	0.329	0.875	0.392	0.242	0.242	0.308	1.625
Chlorine . . . . .	0.202	0.249	0.218	0.028	0.148	0.001	0.102
Nitrogen . . . . .	0.897	1.605	1.714	0.661	0.951	0.937	0.732

The roots of 100 plants contained:—

Grams	1st period	2nd period	3rd period	4th period	5th period
Organic matter . . . . .	6.158	16.669	23.027	25.677	20.764
Ash . . . . .	2.006	1.739	1.663	1.873	1.538
Dry substance . . . . .	8.164	18.408	24.690	27.550	22.302
Potash . . . . .	0.230	0.165	0.167	0.159	0.079
Soda . . . . .	0.118	0.114	0.125	0.106	0.087
Lime . . . . .	0.652	0.648	0.588	0.611	0.645
Magnesia . . . . .	0.108	0.072	0.047	0.039	0.033
Ferric oxide . . . . .	0.053	0.043	0.046	0.079	0.075
Phosphoric acid . . . . .	0.197	0.161	0.128	0.097	0.077
Silica . . . . .	0.590	0.517	0.538	0.715	0.483
Chlorine . . . . .	0.050	0.041	0.031	0.039	0.035
Nitrogen . . . . .	0.237	0.438	0.490	0.642	0.583

From these data given the following table was constructed:—

	100 Plants							Hence there was found, at the time of harvest, more (+) or less (—) than was supplied in	
	contained			contained at the period of maturation					
	A In the manure	B In 38·3 kils. of sand	Total of A + B	In the grain	In the straw and chaff	In the root	Total	A	A + B
Potash . . . . .	1·778	0·048	1·826	0·235	0·495	0·079	0·809	— 0·989	— 1·017
Soda . . . . .	—	0·993	0·993	0·012	0·104	0·087	0·203	+ 0·203	— 0·790
Lime . . . . .	3·733	1·740	5·473	0·087	1·045	0·645	1·777	— 1·956	— 3·686
Magnesia . . . . .	0·267	0·757	1·026	0·149	0·168	0·033	0·350	+ 0·083	— 0·676
Ferric oxide . . . . .	3·333	10·226	13·559	0·031	0·137?	0·075	0·243?	— 3·090?	— 13·616?
Phosphoric acid . . . . .	1·183	0·319	1·502	0·566	0·159	0·077	0·802	— 0·381	— 0·700
Silica . . . . .	2·500	1·165	3·665	0·308	1·625	0·483	2·416	— 0·084	— 1·349
Chlorine . . . . .	0·295	?	0·295	0·001	0·102	0·035	0·138	— 0·157	— 0·157
Sulphuric acid . . . . .	0·533	0·086	0·619	?	?	?	?	?	?
Nitrogen . . . . .	1·867	—	1·867	0·937	0·732	0·585	2·252	+ 0·385	+ 0·385

\* No account is here taken of the ash-constituent in the seed sown.

Deducting 0.108 gram of nitrogen supplied in the seed from the above 0.385 gram, there remains 0.277 gram nitrogen derived from the nitrogenous compounds in the air.

The daily increase in the amount of ash was in the first period 0.386, in the second period 0.116, in the third period 0.078, in the fourth period 0.026, in the fifth period 0.012; whilst that of nitrogen was in the first period 0.113, in the second period 0.083, in the third period 0.011, in the fourth period 0.006, and in the fifth period 0. Consequently, the most active assimilation of mineral matters and of nitrogen occurred during the early stages of growth, comprehending, according to the experiments, the first third of the whole period of vegetation.

The relative proportions of phosphoric acid and nitrogen in the grain were also determined, and it was found that in the unripe state the proportions are 1 : 1.72, and in the ripe grain 1 : 1.66. As regards the migration of nutriment from the root upwards, and from the stalks and leaves into the seed, the following was established. A translation of potash from the root into the upper portion of the plant appears to occur during the third period, and of phosphoric acid and magnesia during the whole period of vegetation. In the fifth period the nitrogen decreased in the root and increased in the aerial portion of the plant. The absolute amount of nitrogen was markedly less in the aerial part of the plant during the period when the seed was forming (fourth period), and higher in the root, than during the preceding stage of development. A passage of potash from the upper part of the aerial portion of the plant into the grain was noted in the fourth period. When the grain ripened, magnesia, phosphoric acid and nitrogen were given up to the seed.

As regards the increase of mineral matters, it was established that this is greatest during the first period. Lime, phosphoric acid, and silica increased up to the time of maturity of the seed; magnesia and soda up to the time of formation of the grain. After the third period, the potash underwent a decrease, and the chlorine after the second period; and this, at the time of the ripening of the grain, had gone on to such a degree that of the former only 72 p. c., and of the latter only 48 p. c. of the maximum amount remained. The magnesia slightly decreased after the fourth period.

**BASALT.** F. Zirkel (*Jahrbuch f. Mineralogie*, 1870, 358; *Jahresh. f. Chem.* 1870, 1361), divides basalts, according to their microscopic constituents, into the following classes: (1) *Felspathic basalts*, which are the most frequent, and consist mainly of triclinc felspar and augite, always associated with magnetic and titaniferous iron, often with olivine and nepheline, never with leucite.—(2) *Leucitic basalts*, containing white leucite, augite, olivine, and magnetic iron ore, with nepheline always subordinate. (3) *Nepheline basalts*, composed of nepheline, augite, olivine and magnetic iron ore; frequently also with leucite, more rarely with felspar.

**BAUXITE or BEAUXITE.** The bauxite occurring in the neighbourhood of Béaux (Bouches du Rhône) is largely employed for the preparation of aluminium and alumina. There are two varieties of it, distinguished as ferruginous and aluminiferous; in the former the ferric oxide varies from 25 to 60 p. c. A ferruginous bauxite from the neighbourhood of Nas de Gilles yielded by smelting 42 p. c. iron, and was found by analysis to contain 4 p. c. silica, 18 alumina and titanio oxide, 60 ferric oxide, and 18 water with lime. The aluminiferous bauxite consists, according to five analyses by G. Sainte-Claire Deville, of—

	I.	II.	III.	IV.	V.
Silica . . . . .	20.7	2.8	4.8	—	2.0
Titanium . . . . .	3.2	3.1	3.2	—	1.6
Ferric oxide . . . . .	3.8	25.3	24.8	34.9	48.8
Alumina . . . . .	58.1	57.6	55.4	39.3	33.2
Calcium carbonate . . . . .	trace	0.4	0.2	12.7	5.8
					(corandum)
Water . . . . .	14.2	10.8	11.6	23.1	8.6
	100.0	100.0	100.0	100.0	100.0

I. and II. from Béaux; III. from Allach, near Marseilles; IV. from Béaux; V. from Calabria.

Both varieties of bauxite are compact, earthy, and pisolithic.

The bauxite in the neighbourhood of Béaux is situated between the lowest zone of the tertiary formation and the upper chalk; its origin in this new cretaceous zone is attributed to mineral springs (Coquand, *Bull. Soc. géol. de France*, xxviii. 98; *Jahresh. f. Mineralogie*, 1871, 940).

Nine French bauxites analysed by Siemens (*Chem. Soc. J.* [2] xi. 673) gave the following average result:—

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O
Raw . . . .	3.5	59.2	24.5	12.1 = 99.3
Calcined . . . .	4.01	67.89	28.09	— = 100.19

Eight other samples gave on the average:

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O
Raw . . . .	1.75	59.50	45.50	12.67 = 99.32
Calcined . . . .	2.02	45.53	52.45	— = 100.02.

Irish bauxite analysed by Siemens gave:

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	TiO <sup>2</sup>	H <sup>2</sup> O
Raw . . . .	3.5	35.0	38.0	2.0	21.5 = 99.0
Calcined . . . .	4.45	44.48	48.0	2.54	— = 99.87

Bauxite (or Wocheinite) containing a larger proportion of alumina is found on the Wochein in Carniola. The following are analyses of a dark red, and a light red variety by E. Drechsel (*Dingl. polyt. J.* cciii. 479).

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O	K <sup>2</sup> O	Na <sup>2</sup> O	Li <sup>2</sup> O	TiO <sup>2</sup>
Dark . . . .	4.15	63.16	23.55	8.34	0.79			trace = 99.99
Light . . . .	4.25	72.87	13.49	8.50	0.78			trace = 99.89

Bauxite from the same locality analysed by Siemens gave:

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	CaO	MgO	SO <sup>2</sup>	P <sup>2</sup> O <sup>5</sup>	H <sup>2</sup> O
Raw . . . .	6.29	64.24	2.40	0.85	0.38	0.20	0.46	25.74 = 100.52
Calcined . . . .	8.40	85.88	3.20	1.13	0.50	0.26	0.51	— = 99.88

Bauxite forms an excellent material for the lining of furnaces which have to bear an intense heat, as in Siemens' rotatory furnace. A series of experiments made by Siemens to form solid lumps by using different binding materials, have shown that 3 p. c. of argillaceous clay suffices to bind the bauxite powder previously calcined. To this mixture about 6 p. c. of plumbago powder is added, which renders the mass practically infusible, because it reduces the ferric oxide contained in the bauxite to the metallic state. Instead of plastic clay as the binding agent, water-glass or silicate of soda may be used, which has the advantage of setting into a hard mass, at such a comparatively low temperature as not to consume the plumbago in the act of burning the brick. When the lining is completed, the interior of the bricks is preserved against oxidation, by fluid cinder added to bind them together, which prevents contact with the flame. A bauxite lining of this description resists both the heat and fluid cinder in a very remarkable degree. A rotative furnace at Siemens' Sample Steel Works at Birmingham was lined partly with bauxite and partly with carefully-selected plumbago bricks. After a fortnight's working the brick lining was reduced from 6 inches to less than half an inch, whereas the bauxite lining was still 5 inches thick and perfectly compact. Moreover, the bauxite, when exposed to intense heat, is converted into a solid mass of emery of such extreme hardness that it can hardly be touched by steel tools, and is capable of resisting mechanical as well as the calorific and chemical actions to which it is exposed. The bauxite used for this lining contained 53.62 p. c. alumina, 42.26 ferric oxide, and 4.12 silica.

**BEANS.** The following observations on the influence of light on the germination of the kidney-bean (*Phaseolus vulgaris*) have been made by H. Karsten (*Landw. Versuchs-Stationen*, xiii. 176).

The beans selected were as uniform as possible. After weighing, they were allowed to germinate between wet blotting-paper, and the shells removed. When the roots were sufficiently developed, the beans were supported on gauze, with their roots in distilled water. One series was then exposed to direct sunlight, the roots only being shaded; the other series was kept wholly in the dark. Each bean was harvested as soon as the second leaf began to make its appearance; this occurred in 15-20 days in sunlight, and in 25-30 days in darkness. The number of beans germinated in this manner was 564.

The plants grown in the dark were of far greater length than those exposed to sunlight. The proportion of the various parts is shown in the following table; the figures represent the yield of 1,000 grams of air-dried beans, containing 745 grams of dry matter free from husks:—

	Leaves	Stalks of first leaves	Internodes	Roots	Cotyledons	Total plants	Original beans
Light {fresh weight . .	722.0	115.0	615.0	1038.0	1551.0	4041.0	1000
{dry weight . .	114.6	12.3	78.3	87.0	334.3	626.5	745
Darkness {fresh weight	134.0	293.0	2027.0	832.0	1582.0	4886.0	1000
{dry weight .	22.6	19.6	174.0	62.4	277.7	556.2	745

The loss of weight in germination is seen to be greatest in the dark; the leaves had not in this case the nutritive action which they probably exercised in sunlight.

A separate chemical analysis was made of each part of the young plants. The composition of the dried, entire plants is compared below with that of the original beans, 1,000 grams of air-dried beans serving as before for comparison:—

	Composition of original beans	Grown in light		Grown in darkness	
		Composition	Gain or loss per cent.	Composition	Gain or loss per cent.
Crude fat . . . . .	19.08	19.82	+ 3.92	16.00	— 16.09
Sugar . . . . .	8.75	13.93	+ 59.16	8.42	— 3.82
Gummy matter . . .	84.92	105.89	+ 24.69	78.60	— 7.45
Starch . . . . .	146.01	74.40	— 49.04	62.21	— 57.41
Cellulose . . . . .	17.47	57.97	+ 231.84	65.57	+ 275.84
Protein . . . . .	185.79	160.46	— 13.63	168.69	— 9.24
Ash . . . . .	30.17	34.85	+ 15.49	35.43	+ 17.44
Non-nitrogenous mat- ter undetermined }	252.81	159.20	— 37.03	121.31	— 52.01
Total dry matter .	745.00	626.52	— 15.90	556.23	— 25.31

The water in which the young plants grew was found to contain but a trace of solid matter.

**BEET.** Numerous analyses of sugar-beets grown in England and Ireland in 1869 and 1870, have been made by Dr. Voelcker, and published in the *Journal of the Royal Agricultural Society*, [2] vii. 60. The season of 1870 proved more favourable to the formation of sugar than 1869. Samples grown in 1869 gave—English roots, 8–12 p. c. sugar; Irish roots, 6–11 p. c. sugar. Samples of the crop of 1870 gave—English roots, 9–13.3 p. c. sugar; Irish roots, 10–14.8 p. c. sugar. Large roots are shown to be more watery, and contain less sugar than smaller roots. Liberal manuring increases the bulk of the crop, but injures its quality; one effect being the increase of albuminous and saline matters, the presence of which prevents the crystallisation of a certain percentage of the sugar. The part of the root grown above the ground contains less sugar and more nitrogen than the buried portion: hence the advisability of deep culture of the soil. The following are characteristic analyses:—

	Lavenham, 1869. Average of fifteen lots	Large root from Buscot, 1869	Single root, Berkshire, 1869		Viewmont, Kilkenny, 1870. Average of ten roots
			Upper portion	Lower portion	
Water . . . . .	82.46	91.50	87.20	86.05	77.76
Sugar . . . . .	11.06	3.89	4.24	8.05	14.73
Albuminous com- pounds . . . . }	.81	1.04	2.39	.82	1.66
Pectin, &c. . . .	.66	.36	.40	.89	.69
Crude fibre . . .	3.87	1.90	3.73	3.08	4.86
Ash . . . . .	1.14	1.31	2.04	1.11	.80
	100.00	100.00	100.00	100.00	100.00
Weight . . . . .	—	12.25 lbs.	.31 lb.	2.5 lbs.	1.53 lb.

The distillation of spirit from beetroot is largely practised on the Continent; it has been recently commenced in England on a great scale by Mr. Campbell, of Buscot. This manufacture turns to profit the molasses of the sugar-factories, and utilizes the crops of bad seasons, when the percentage of sugar is below that (about 8 p. c.) required for profitable extraction. It is considered by many more remunerative than the manufacture of sugar, and is certainly more consistent with high farming, the albuminous and saline matters favoured by liberal manuring being no obstacle to the production of spirit.

Beetroot is prepared for fermentation by one of three processes:—I. The roots are pulped or sliced, mixed with a small quantity of sulphuric acid, then pressed, and the juice is fermented. II. (Champonoi's method.) The roots are sliced, and treated with hot wash acidulated with sulphuric acid; no press is used, the sugar being extracted by displacement. III. (Löplay's method.) The slices of beetroot are placed in vats, and fermented without previous treatment. The residual pulp from each of these methods is used as cattle food.

Beetroot spirit is very apt to be contaminated with fusel oil, but the use of good distilling apparatus (as that of the Messrs. Saralle) effectually removes this impurity.

Since sugar-beet contains far more nutritive matter than the best mangolds, it may frequently be of more value for feeding purposes than for the sugar or spirit manufacture.

The distribution of mineral substances by the root of beet has been studied by Corenwinder (*Compt. rend.* lxxiii. 95). Samples of Italian beetroot from Modena, Milan, Bologna, and Vicenza were examined, and their composition compared with that of French beetroot from the departments of Nord and Pas-de-Calais. The Italian beets were poor in sugar and contained much saline matter. 1 litre of juice yielded 52.5 to 85 grams of sugar and 10.2 to 16.2 grams of mineral salts. The juice of the French beets gave 90.7 to 132.4 grams of sugar, and 7.3 to 8.7 grams of salts per litre. The density of the juice from the Italian beets was comparatively high. Density is not a safe indication of saccharine value, owing to the disturbing influence of the saline ingredients. The amount of potash in the Italian beets was very considerable. Taking all the samples into account, it appears that the proportion of potash bore an inverse relation to the amount of sugar. Some of the samples of Italian beet contained a large proportion of chlorides; in these cases the proportion of soda was also excessive. The following analyses show, however, that sodium is taken up by the plant in other forms besides that of chloride. The analyses were made on three samples of French beet grown in the same field with different manures; the quantities refer to 1 litre of juice. (See Table on opposite page.)



	No manure	Chemical manure	Earth-nut cake
	gram	gram	gram
Chloride of sodium . . . . .	1.238	.798	1.611
Potash . . . . .	2.308	2.327	2.315
Soda . . . . .	.902	1.125	.699
Lime . . . . .	.216	.160	.271
Magnesia . . . . .	.322	.293	.231
Sulphuric acid . . . . .	.406	.201	.182
Phosphoric acid . . . . .	.581	.657	.144
	5.973	5.661	5.853

On the results of manures applied to beetroots, see also Czech (*Dingl. polyt. J.* cc. 499), and Sestini a. Del Torre (*Gazzetta chimica italiana*, iii. 190; *Chem. Soc. J.*, xxvi. 1254).

**BELLIS.** The flower-heads of the common daisy (*Bellis perennis*) contain an iron-greening tannin, malic, tartaric, oxalic, and acetic acid, a soft resin (antholeucin), a yellow colouring matter (anthoxanthin), together with chlorophyll, albumin, &c. (J. B. Enz, *Viertelj. f. Pharm.* xix. 1).

**BENZAMARONE.**  $C^9H^{10}O^4$ .—A body formed by the prolonged action of alcoholic potash at ordinary temperatures or deoxybenzoïn; 100 grams of deoxybenzoïn digested with a solution of 104 grams potassium hydrate in a litre of 90 p. c. alcohol, yielded about 20 grams of crystallised benzamarone in a fortnight. Benzamarone crystallises in needles, melts at  $225^\circ$ , dissolves in 157 parts of boiling, and 1130 parts of cold alcohol of 77 p. c. in 10 pints of boiling benzene and 35 pints of boiling acetic acid. When heated for some time with alcoholic potash, it is resolved into about equal parts of deoxybenzoïn and amaric acid (p. 55), also benzoic acid and a small quantity of resinous matter (Zinin, *Zeitschr. f. Chem.* vii. 127).

**BENZAMIDE.**  $C^7H^7NO$ .—This compound forms monoclinic crystals, in which the axes  $a : b : c = 0.228404 : 1 : 1.06827$ , and the angle of the inclined axes  $b c = 89^\circ 22'$ .—Principal angles  $OP : \infty P\infty = 90^\circ 38'$ ;  $+P\infty : \infty P\infty = 135^\circ 10'$ ;  $\infty P : \infty P = 154^\circ 16'$  in the orthodiagonal principal section. Observed forms (Fig. 4):

$$\begin{array}{ccccc} \infty P & \infty P\infty & OP & +P\infty & +\frac{1}{2}P\infty. \\ i & a & b & m & l \end{array}$$

The crystals obtained by fusion are almost always twins, whose twin-axis is the principal axis, and face of combination  $\infty P\infty$ . A solution of benzamide in ether often yields simple crystals together with twins: an alcoholic solution for the most part, only simple crystals. The crystals are sometimes prismatic, elongated in the direction of  $\infty P$ ; sometimes they have also short prismatic forms. Occasionally they are tabular parallel to  $\infty P\infty$ , and lengthened in the direction of the orthodiagonal. They cleave perfectly parallel to  $\infty P\infty$ , less easily parallel to  $+P\infty$ . The faces  $\infty P$  and  $\infty P\infty$  have a strong lustre;  $OP$ ,  $P\infty$ , and  $+\frac{1}{2}P\infty$  are more or less striated. The crystals are colourless, seldom quite transparent.

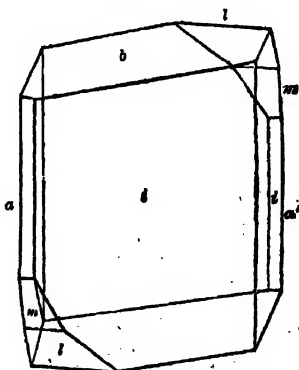
The plane of the optic axes coincides with the clinodiagonal principal section. The two principal directions of vibration are so situated in this plane that one runs nearly parallel to  $+P\infty$ , the other nearly at right angles to it. The first of these directions is inclined to  $\infty P\infty$  at the angles  $49^\circ 53'$  and  $130^\circ 7'$ , the obtuse angle being turned towards  $OP$ . Dispersion  $\rho < v$ . L. Klein, *Ann. Ch. Pharm.* clxvi. 184).

Benzamide heated for several hours with bitter almond oil forms benzylbenzamide,  $C^{11}H^{11}N^2O^2$ .

2nd Sup.

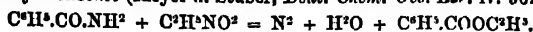
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Fig. 4.



$2H = 100^\circ 15'$  red;  $102^\circ 10'$  blue

Benzamide heated in sealed tubes to about 120° with ethyl nitrite, yields nitrogen, water, and ethyl benzoate (Meyer a. Stüber, *Deut. Chem. Ges. Ber.* iv. 962).



Benzamide unites with chloral, forming the compound  $\text{C}^6\text{H}^5\text{Cl}^3\text{NO} = (\text{CCl}^3\text{CHO}).\text{C}^6\text{H}^5\text{CONH}^2$ , which melts at 150°–151° (Wallach, *ibid.* v. 251).

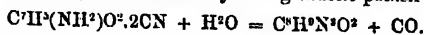
*Trichlorobenzamide*,  $\text{C}^6\text{H}^3\text{Cl}^3\text{CO.NH}^2$ , produced by heating trichlorobenzoyl chlorido with ammonia, crystallises in small needles, melting at 176°, easily soluble in alcohol and in ether (Salkowski, *Ann. Ch. Pharm.* clxiii. 1).

*Diamidobenzamide*,  $\text{N}^{\text{H}^2}\{\text{C}^6\text{H}^4(\text{NH}^2)^2\text{O} \text{ or } \text{C}^6\text{H}^3(\text{NH}^2)^2\text{CONH}^2$  (Muretow, *Zeitschr. f. Chem.* [2] vi. 642). Obtained by reduction of dinitrobenzamide. For this purpose dinitrobenzoic acid is gently heated with excess of phosphorus pentachloride till reaction begins, and when it is over the cooled liquid is poured into strong ammonia. The dinitrobenzamide thus formed crystallises in pale yellow laminae, exhibiting the properties described by Voit (i. 541). Melting point 177° (183° according to Voit). A boiling aqueous solution of this nitro-amide, mixed with ammonium sulphide, left to itself for 24 hours, then boiled up, filtered from sulphur and evaporated over the water-bath, yields the diamido-amide in the form of a brown-black syrup, the crystallisation of which is greatly facilitated by the introduction of a crystal of the compound previously prepared. The crystals thus obtained are black, and cannot be decolorised by animal charcoal. The solution of the amide, which is nearly colourless at first, turns yellow after a while, and deposits yellow crystals.

Diamidobenzamide forms large, four-sided, brownish-yellow, needle-shaped crystals, slightly soluble in cold, very easily in hot water. The aqueous solution turns brown in contact with the air, probably from oxidation. Its *hydrochloride*,  $\text{C}^6\text{H}^3(\text{NH}^2)^2\text{NO} \cdot 2\text{HCl}$ , is precipitated from the aqueous solution by hydrochloric acid in white needles having a silky lustre. The *picrate* is a yellow crystalline precipitate, very slightly soluble in water (1 part in 735), and crystallising from the solution in small yellow needles.

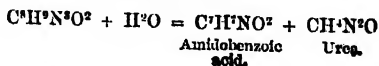
*Diacetyl-diamidobenzamide*,  $\text{C}^6\text{H}^3(\text{NH}^2\text{C}^2\text{H}^3\text{O})^2\text{CONH}^2 + 2\text{H}^2\text{O}$ , is obtained by treating the amide with acetic anhydride, and recrystallising the product from water. It forms long, thin, colourless needles, slightly soluble in cold, freely in hot water. From alcohol, in which it is still more soluble, it separates in tufts of needles. Melts above 265°, and then solidifies in the vitreous form. Gives off its water of crystallisation at 100° (Muretow).

**BENZOREATINE.**  $\text{C}^6\text{H}^5\text{N}^2\text{O}^2$  (Griess, *Deut. Chem. Ges. Ber.* i. 191; iii. 703; *Zeitschr. f. Chem.* iv. 725; vi. 728). A base produced by boiling cyanide of amidobenzoic acid (1st Suppl. 317) with moderately strong caustic potash:—

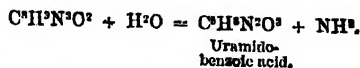


The solution, when it has become colourless, is left to cool and then mixed with a large excess of acetic acid; the base is thereby precipitated almost completely, and may be purified by repeated crystallisation from hot water, with addition of animal charcoal.

Benzcreatine crystallises in thin, white, shining, right-angled, four-sided plates containing 1 mol. water: it gives off its water of crystallisation at 120°, melts at a higher temperature, and volatilises gradually without decomposition. It is moderately soluble in hot water, but crystallises out almost completely on cooling; in boiling alcohol it dissolves very slowly, and crystallises therefrom in short thick needles; it is almost insoluble in ether, quite insoluble in ammonia. When boiled for a long time with baryta-water, it is resolved into amidobenzoic acid, urea, ammonia, and uramido-benzoic acid, according to the following equations:—



and

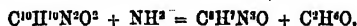


Benzcreatine forms salts with mineral acids, but does not unite with acetic acid. The *hydrochloride*,  $\text{C}^6\text{H}^5\text{N}^2\text{O}^2\text{HCl}$ , crystallises in somewhat elongated, rectangular four-sided plates, very soluble in hot, sparingly soluble in cold water; it is precipitated from its concentrated aqueous solution by hydrochloric acid. The *platinocarbonate*

$2(C^6H^5N^3O^4.HCl).PtCl_4$ , crystallises in yellow spiculae, moderately soluble in hot, sparingly in cold water.

Benzereatine was at first regarded by Griess as a compound of 2 mol. amidobenzoic and 1 mol. oxamide:  $2C^6H^5(NH^2)O^2 + C^6H^5N^3O^2 = C^{12}H^{10}N^4O^4$ ; but later experiments have established the formula  $C^{12}H^{10}N^4O^2$ , which gives very nearly the same percentage of carbon and hydrogen as  $C^{12}H^{10}N^4O^4$ , or  $C^6H^5N^3O^4$ .

**BENZEREATINE.**  $C^{12}H^{10}N^4O$  (Griess, *Proc. Roy. Soc.* xviii. 89; *Deut. Chem. Ges. Ber.* ii. 415; *Zeitschr. f. Chem.* [2] v. 574).—A base produced by heating the compound  $C^{12}H^{10}N^4O^2$ —resulting from the action of cyanogen on anthranilic (meta-amidobenzoic) acid—with alcoholic ammonia for some days in a sealed tube placed in the water-bath:



It crystallises in nacrous laminae, nearly insoluble in water, slightly soluble in boiling alcohol. Its *nitrate* forms white narrow laminae, nearly insoluble in alcohol; the *platinochloride*,  $2(C^6H^5N^3O.HCl).PtCl_4$ , crystallises in thick yellow needles.

**BENZENE.**  $C^6H^6$ . *Physical Properties.*—Benzene crystallises in trimetric pyramids, having their axes in the proportion:—

$$a : b : c = 0.801 : 1 : 0.770$$

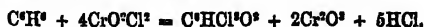
(Groth, *Zeitschr. f. Chem.* [2] vi. 553). Its index of refraction (in the liquid state) at  $9^\circ$  is 1.4593 for the line A, 1.5050 for D, 1.5307 for H (Gladstone, *Chem. Soc. J.* [2] vii. 101).

*Reactions.* Benzene, heated with sulphur in sealed tubes to  $400^\circ$ – $500^\circ$ , forms a product which dissolves for the most part in alcohol, and separates therefrom in long needles and crystalline crusts, smelling like diphenyl, and having also the disagreeable odour of volatile sulphur-compounds. Much hydrogen sulphide escapes on opening the tubes (F. Schulze, *Deut. Chem. Ges. Ber.* iv. 33).

Benzene and potassium heated together in a sealed tube to  $240^\circ$ – $250^\circ$ , combine into a black mass, which appears blue in thin layers, explodes very easily when dry, and is violently decomposed by water. The gradual action of water on it gives rise to diphenyl (Abeljung, *Deut. Chem. Ges. Ber.* v. 1027).

Berthelot found, in opposition to Harnitzky, that carbonyl chloride does not act on benzene either at ordinary or at higher temperatures (1st *Suppl.* 262). On repeating his experiments he finds that no action takes place at  $280^\circ$ ; but that when liquid carbonyl chloride is heated with 5 or 6 vol. benzene to  $320^\circ$  for 36 hours, the carbonyl chloride disappears almost entirely, being replaced by a mixture of hydrogen chloride and carbon monoxide. Part of the benzene is at the same time charred, but no chrysene is formed; only traces of a volatile, strong-smelling hydrocarbon (? phenylene), and not a trace of benzoyl chloride. Neither is this last compound formed when benzene and carbonyl chloride are heated together for 20 hours to  $280^\circ$ . That this negative result is not due to decomposition of the benzoyl chloride by heat, is shown by the fact that this compound may be heated to  $290^\circ$  for 120 hours without perceptible decomposition. Berthelot concludes, therefore, that benzoyl chloride is not formed by the action of carbonyl chloride on benzene at any temperature (*Bull. Soc. Chim.* [2] xiii. 391).

Chromic oxychloride acts with great violence on benzene, and if the two bodies are brought directly in contact, nothing is formed but resinous products; but if the benzene be diluted with an equal volume of glacial acetic acid (which is not acted upon by chromic oxychloride), a solution of chromic oxide diluted with 2 vol. glacial acetic acid carefully dropped into it as long as any action takes place, and the liquid mixed with a large quantity of water, the benzene rises to the surface in the form of a golden-yellow liquid. On removing this layer, repeatedly agitating the green solution with fresh portions of benzene as long as they acquire a yellow colour, and distilling the united portions of benzene till crystals begin to separate in the retort, the remaining liquid solidifies on cooling to a laminar crystalline mass of trichloro-quinone, which may be purified by recrystallisation from hot alcohol. The reaction is:



If the chromic oxychloride contains free chlorine, tetrachloro-quinone is likewise formed, together with an oil not yet examined (Carstanjen, *J. pr. Chem.* cvii. 31).

*Benzene Hexachloride*,  $C^6H^2Cl^4$ .—According to Zachar Heyn (*Zeitschr. f. Chem.* [2] vii. 293), this compound is most readily obtained by acting on boiling benzene with

excess of chlorine, evaporating off the unaltered benzene, pressing the crystals which separate on cooling to free them from mother-liquor, and recrystallising from alcohol or benzene. It melts at  $157^{\circ}$  (according to Mitscherlich, at  $132^{\circ}$ ; according to Laurent, at  $135^{\circ}$ - $140^{\circ}$ ). According to Vohl (*Zeitschr.* [2] iii. 122), it forms a crystalline compound with fuming nitric acid. Heys, however, finds that it is not in the least altered either by boiling with fuming nitric acid for many hours, or by treating it with a hot mixture of nitric and sulphuric acid. Hence it would appear that the formation of nitro-compounds in the aromatic group depends upon the double linking of the carbon-atoms; it is possible also that the chlorine-atoms may influence the adjacent hydrogen and prevent their replacement by  $\text{NO}^2$ .

When the hexachloride is heated to  $150^{\circ}$  with alcoholic potassium acetate, much potassium chloride is formed; on cooling, the filtrate deposits colourless crystals, insoluble in water, sparingly soluble in cold alcohol, but readily dissolved by boiling alcohol; these crystals melt at  $250^{\circ}$ . At the same time a fluid compound is produced, probably trichlorobenzene.

### *Constitution of Benzene.*

Kekulé's theory of the constitution of benzene and its compounds and derivatives has been explained in the *First Supplement* to this Dictionary (pp. 193-215). It is there shown that the ring-formula of benzene, in which the carbon-atoms are supposed to be linked together by one and two combining units alternately, affords a satisfactory explanation of all the best established facts relating to the compounds of the aromatic group, and in particular, that it explains, more clearly than any other yet proposed as a substitute for it, the remarkable fact, that benzene, which for the most part exhibits the characters of a saturated molecule, is capable, under certain circumstances, of taking up, without substitution, 2, 4, or 6 atoms of a univalent radicle, and forming such compounds as hexachlorobenzene,  $\text{C}_6\text{H}_2\text{Cl}_6$ , just as ethylene  $\text{C}_2\text{H}_4$ , which in the free state is also a saturated molecule, can take up 2 atoms of chlorine to form the compound  $\text{C}_2\text{H}_4\text{Cl}_2$ .

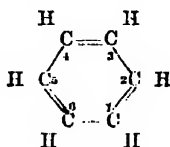
The chief objections which have been raised against Kekulé's benzene formula are the two following:—1. That, since according to this formula, the six atoms of hydrogen in benzene are of equal value, only one pentachlorobenzene is possible, whereas two are said to exist. This objection cannot, however, be regarded as of much weight, inasmuch as the experimental demonstration of the existence of two such compounds is still incomplete (see p. 14).

The second objection, which at first sight appears of more importance, is the following:—It is argued that those di-derivatives, in which the substituting radicles occupy contiguous positions, should differ according as the replacement has taken place on adjacent carbon-atoms united by one affinity ( $\text{C}-\text{C}$ ), or by two affinities ( $\text{C}=\text{C}$ ); the so-called 1 : 2 derivatives should therefore be isomeric, not identical, with the 1 : 6 derivatives, so that four di-derivatives of benzene are possible, whereas hitherto at most three have been obtained. Such a difference, if it existed, would perhaps be too slight to be recognisable; and Kekulé is of opinion that the assumption of its existence arises rather from the kind of diagram employed to represent the benzene molecule, than from the ideas of which this diagram affords but an imperfect representation. To show that no such difference need be supposed to exist, he brings forward the following hypothesis as to the mode of motion of the atoms in the benzene molecule:—

The atoms in the systems which we term molecules must be considered as in continuous movement; no explanation, however, has hitherto been given as to the nature of the intramolecular motion. A planetary motion appears inadmissible in face of the law of the linking of atoms (*Verkettung*) now recognised in chemistry. The motion must indeed be of such a nature that all the atoms of the system retain the same relative arrangement, or in other words, that all the atoms return to a mean position of equilibrium. The most probable assumption then appears to be that the separate atoms of the system, possessing an essentially rectilinear motion, strike one against the other and, being elastic bodies, then recoil. On this supposition the term *quantivalence* (atomicity) acquires a mechanical signification; denoting, in fact, the relative number of contacts which occur in the unit of time between the atoms. In the same time that the univalent atoms of a monatomic molecule strike against each other once, the bivalent atoms of a diatomic molecule come twice in contact at the same temperature. In a molecule consisting of one bivalent and two univalent atoms the number of contacts in the unit of time is equal to two in the case of the bivalent atom, and to one in the case of each univalent atom. When two atoms of carbon are united by one affinity of each, they strike against each other once in the unit of time, that is to say, in the time during which the univalent hydrogen makes one complete vibration; during the same unit of time they also each encounter three other (univa-

lent) atoms. Carbon atoms united by two affinities of each, strike against each other twice, and during the same time come only twice in contact with other atoms.

Applying this view to benzene, Kekulé's formula is an expression of the following conception:—Each carbon-atom strikes against two other carbon-atoms during the unit of time, once against the one and twice against the other. In the same unit of time it also comes once in contact with the hydrogen-atom, which during the same period makes one complete vibration. Representing benzene by the hexagon formula, and having regard to any one of the six atoms of carbon, that denoted by 1 for example:—



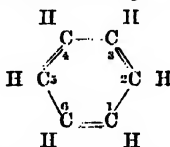
the contacts of this atom during the first unit of time may be thus represented:—

1. 2, 6, h, 2,

in which h denotes hydrogen. The vibrations of the same atom during the second unit of time are then as follows:—

2. 6, 2, h, 6.

The contacts during the first period being represented by the above formula, those occurring during the second unit of time are represented by the following:—



The same carbon-atom is therefore, during the first unit of time, united by two affinities to one of the contiguous carbon-atoms; during the second, by two affinities to the other contiguous atom.

The number of contacts made by the carbon-atom during the first two units of time—the vibrations completed during these intervals being periodically repeated—are then as follows:—

2, 6, h, 2, 6, 2, h, 6,

from which it is evident that each carbon-atom strikes against each of the two carbon-atoms upon which it impinges, an equal number of times, or, in other words, that it bears the same relation to both contiguous atoms. The ordinary benzene formula only represents the contacts made during the first unit of time, and thus it is that the false view has sprung up that di-derivatives in which the radicles occupy the positions 1 : 2 and 1 : 6 respectively must be different. If the above, or some similar conception be correct, it follows that no real difference exists (Kekulé, *Ann. Ch. Pharm.* elxii, 77).

Criticisms of these views have been published by Ladenburg (*Deut. Chem. Ges. Ber.* v. 322) and Michaelis (*ibid.* 463).

#### *Orientation of the Substituted Radicles or Lateral Chains in the Di-derivatives of Benzene.*

In the article AROMATIC SERIES in the *First Supplement* it has been explained that the di-derivatives of benzene may be arranged in three isomeric series: the individual members of each of which may be formed one from the other by a series of simple substitutions not involving a complete change in the structure of the molecules, and are therefore supposed to have their lateral chains in similar positions. These series are distinguished by the prefixes *ortho*, *meta*, and *para*: the first including those compounds which may be derived from, or converted into phthalic acid; the second related in like manner to isophthalic acid; and the third to terephthalic acid. It was further explained in the same article that, although the relative positions of the substituted radicles or lateral chains in the three series could not be fixed with certainty, still the facts then ascertained rendered it most probable that the arrangement in the *ortho*-series was

represented by the formula, 1 : 2, in the meta-series, by 1 : 3, and in the para-series by 1 : 4; these three being the only possible arrangements.

Subsequent researches have, in the main, confirmed these views, but at the same time have somewhat modified them so far as regards the individual compounds belonging to each series.

The derivatives in which the position of the lateral chains is most easily determinable, are the dicarbon-acids, phthalic, isophthalic, and terephthalic, represented by the formula  $C^6H^4 \begin{Bmatrix} CO^2H \\ CO^2H \end{Bmatrix}$ . Of these, phthalic acid is inferred to belong to the 1 : 2 series: first, on account of its formation from naphthalene; secondly, from

the readiness with which it is converted into an anhydride  $C^6H^4 \begin{Bmatrix} CO \\ CO \end{Bmatrix} O : a$

property which indicates the contiguity of the two carboxyl groups in phthalic acid, and is not exhibited by isophthalic or terephthalic acid. Isophthalic acid is formed by oxidation of isoxylene,  $C^6H^4 \begin{Bmatrix} CH^3 \\ CH^3 \end{Bmatrix}$ , which is a derivative of mesitylene. Now, mesitylene has been shown to be a symmetrically constituted trimethyl-benzene,  $C^6H^3(CH^3)^3$ , having its three methyl-groups in the positions 1 : 3 : 5; consequently, the two methyls in isoxylene, and therefore the two carboxyls in isophthalic acid, must be in the positions 1 : 3. For terephthalic acid, therefore, there remains only the arrangement 1 : 4 (*1st Suppl.* 198).

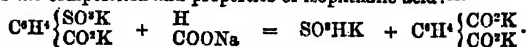
Another compound in which the relative position of the lateral chains may be determined with comparative facility is hydroquinone,  $C^6H^4 \begin{Bmatrix} OH \\ OH \end{Bmatrix}$ , the conversion of

which, by oxidation into quinone,  $C^6H^4 \begin{Bmatrix} O \\ O \end{Bmatrix}$ , indicates that the two hydroxyls

contained in it occupy contiguous positions (1 : 2). Of the two other dioxybenzenes or oxyphenols, viz. pyrocatechin and resorcin, the last is derived from compounds which are convertible more or less directly into terephthalic acid, and is therefore a 1 : 4 compound, while the second is similarly related to compounds of the isophthalic series, and is therefore a 1 : 3 compound.

The constitution of other di-derivatives of benzene is best determined by their convertibility into one of the three dicarbon-acids, or one of the three oxyphenols.

Oxybenzoic acid and the chloro-, bromo-, amido-benzoic acids, &c., related to it have hitherto been generally regarded as 1 : 2 compounds; while salicylic acid and its congeners, chlorosalicylic, bromosalicylic, anthranilic acid, &c., have been referred to the 1 : 3 series. This view, however, is somewhat at variance with the fact that the formation of anhydrides, or similarly constituted bodies, takes place, not in the first or oxybenzoic acid group, but in the second or salicylic acid group (e.g. salicylide, coumarin). It therefore seems more probable that the 1 : 2 arrangement belongs to this latter group. To decide this question, V. Meyer (*Ann. Ch. Pharm.* clvi. 265) has examined the action of sodium formate on sulphobenzoic acid,  $C^6H^4 \begin{Bmatrix} SO^2H \\ CO^2H \end{Bmatrix}$ , which, according to Barth (*ibid.* cxlviii. 34), yields, by fusion with potash, nothing but oxybenzoic acid, and is therefore a strict analogue of the latter. When equal weights of sodium formate and potassium sulphobenzoate are fused together, the fused mass digested in water, and the aqueous solution, after acidulation, shaken up with ether, an acid is obtained which, when purified by conversion into a barium salt, separation therefrom by hydrochloric acid, and recrystallisation from hot water, melts above  $300^\circ$ , and exhibits the composition and properties of isophthalic acid:—



Since then, isophthalic acid has the two groups,  $CO^2H$ , in the position 1 : 3, it follows that the same relative position of the radicles must exist in sulphobenzoic acid, and therefore also in oxybenzoic acid; and that the other derivatives of benzoic acid (chloro-, bromo-, nitro-, amido-) which are convertible into oxybenzoic acid, must also have their lateral chains in the position 1 : 3, not as hitherto supposed, in the position 1 : 2. This conclusion has been experimentally verified in the case of bromobenzoic acid (produced by heating benzoic acid with bromine and water, or by the action of hydrobromic acid on diazobenzo-amidobenzoic acid: *1st Suppl.* 300): the potassium salt of which, when heated with sodium formate, also yields an isophthalate.

Further, since the para-derivatives of benzoic acid, as shown by Graebe (*Ann. Ch. Pharm.* cxlix. 27), have their lateral chains in the position 1 : 4—inasmuch as para-

bromotoluene, which yields parabromo-benzoic acid by oxidation, is further convertible into terephthalic acid—there remains, for salicylic acid and its congeners, only the position 1 : 2. This view, as already observed, is in accordance with the existence of anhydrides in the salicylic series; and salicylic acid likewise resembles acknowledged 1 : 2 compounds, phthalic acid, for example, in volatilising with vapour of water, whereas oxy-benzoic and paraoxy-benzoic acids do not.

These, however, are but indirect proofs of the existence of salicylic acid as a member of the 1 : 2 series; the following direct proof has lately been given by Fittig u. Ramsay (*Ann. Ch. Pharm.* clxix. 242). Toluene treated with sulphuric acid yields two toluene-sulphonic acids,  $C^6H^4 \begin{Bmatrix} CH^3 \\ SO^2H \end{Bmatrix}$ , the more abundant of which, distinguished

by the sparing solubility of its potassium salt, is known to be the para-compound (1 : 4). The other belongs to the same series as salicylic acid, since by fusion with potash it yields a cresol, which, by the further action of the alkali, is converted into salicylic acid. Now, when this second toluene-sulphonic acid (hitherto regarded as a meta-compound) is distilled with potassium cyanide, the group  $SO^2H$  is replaced by  $CN$ , and tolyl cyanide,  $C^6H^4 \begin{Bmatrix} CH^3 \\ CN \end{Bmatrix}$ , is obtained, which, by treatment with alcoholic potash, is converted into toluic acid,  $C^6H^4 \begin{Bmatrix} CH^3 \\ COOH \end{Bmatrix}$ ; and finally this toluic acid, when treated with chromic acid, is completely oxidised to carbonic acid and water—just like the orthotoluic acid obtained by other methods, whereas metatoluic acid, when similarly treated, is converted into isophthalic acid. Consequently the second toluene sulphonic acid—and therefore also salicylic acid—belongs to the 1 : 2 series.

The constitution of a few other di-derivatives of benzene has been determined by Meyer u. Ador (*Ann. Ch. Pharm.* clix. i.).

Sulphanilic acid,  $C^6H^4NSO^2 = C^6H^4 \begin{Bmatrix} NH^2 \\ SO^2H \end{Bmatrix}$ , is converted by nitrous acid into diazosulphanilic acid; this diazo-acid, heated with hydrobromic acid, yields bromobenzeno-sulphonic acid,  $C^6H^4BrSO^2 = C^6H^4 \begin{Bmatrix} Br \\ SO^2H \end{Bmatrix}$ ; and this last acid, fused with potash, is converted into resorcin, without any admixture of pyrocatechin or hydroquinone. The same brominated sulphuric acid, distilled with potash, yields di-cyanobenzeno  $C^6H^4(CN)^2$ , which by boiling with potash is converted into terephthalic acid. These reactions show that the bromobenzeno-sulphonic acid, and the sulphanilic acid from which it is derived, belong to the para-series.

Sulphanilic acid treated with nitrous acid yields the diazo-derivative,  $C^6H^4 \begin{Bmatrix} N=N \\ SO^2 \end{Bmatrix}$ , which, by boiling with water, is converted into a phenolsulphonic acid,  $C^6H^4 \begin{Bmatrix} OH \\ SO^2H \end{Bmatrix}$ , which yields resorcin when fused with potash, and is therefore identical with the  $\alpha$ -phenolsulphonic (or phenyl-sulphuric) acid, which Kekulé obtained by the action of sulphuric acid on phenol. This acid is, therefore, a para-compound, and affords further evidence of the constitution above assigned to sulphanilic acid.

The following table, drawn up by Meyer, exhibits the constitution of the known di-derivatives of benzene. They are arranged as substitution-products:—

(1) Of Benzoic acid; (2) of Toluene; (3) of Phenol; (4) of Aniline; (5) of Benzenesulphonic acid; (6) of Chloro-; (7) of Bromo-; (8) of Iodo-; and (9) of Nitro-benzene, the substituted radicles being introduced in the following order:  $COOH$ ,  $OH$ ,  $Cl$ ,  $Br$ ,  $I$ ,  $F$ ,  $NO^2$ ,  $NH^2$ ,  $SO^2H$ ,  $CH^3$ .

The less known compounds are characterised by the specification of some special property or mode of formation.

The azo-, diazo-, hydrazo-, thiohydro- ( $SH$ ) derivatives, &c., are not given in the table, since they naturally belong to the same series as the nitro-, amido-, and sulpho-compounds from which they are prepared. Neither are derivatives introduced in which substitution has taken place in the lateral chains, such as—



as their positions in the table are evident without further explanation. For a similar reason, compounds whose lateral chains contain more than one carbon-atom (derivatives of ethyl-, propyl-, vinyl-, &c. benzene) are likewise excluded.

## Di-derivatives of Benzene.

ORTHO-SERIES.*	META-SERIES.	PARA-SERIES.
1:2	1:3	1:4
Phthalic acid.	Isophthalic acid.	Terephthalic acid.
Salicylic acid.	Oxybenzoic acid.	Paraoxy-benzoic acid.
Chlorosalicylic acid.	Chlorobenzoic acid (direct from benzoic acid).	Chlorodracrylic acid (from chlorotoluene).
	Bromobenzoic acid. (direct from benzoic acid).	Bromodracrylic acid (from bromotoluene).
	1:3 Iodobenzoic acid (from diazo-amidobenzoic acid).	Iododracrylic acid (from toluidine).
	Fluobenzoic acid (from diazo-amidobenzoic acid).	
	Nitrobenzoic acid (direct from benzoic acid).	Nitrodacrylic acid (from nitrotoluene).
Anthranilic acid.	Amidobenzoic acid.	Amidodracrylic acid.
	Sulphobenzoic acid.	
1:2 Toluic acid (m. p. 102°).	Isotoluic acid? (m. p. 90°-93°).	1:4 Toluic acid (m. p. 175°; yields terephthalic acid by oxidation).
1:2 Cresol (from 1:2 toluenesulphonic acid; liquid; yields salicylic acid).	1:3 Cresol (from thymol; liquid; yields orthobenzoic acid).	1:4 Cresol (from coal-tar toluidine, &c., solid; yields paraoxybenzoic acid).
1:2 Chlorotoluene (from 1:2 toluidine; burns away when oxidised).	1:3 Chlorotoluene (yields chlorobenzoic acid).	1:4 Chlorotoluene (direct from toluene; yields chlorodacrylic acid).
	1:3 Bromotoluene (liquid; yields bromobenzoic acid).	1:4 Bromotoluene (direct from toluene; solid; yields bromodacrylic acid).
		1:4 Iodobenzene (from toluidine; yields iododacrylic acid).
		1:4 Nitrotoluene (solid; yields nitrodacrylic acid).
Iodobenzene (from pseudotoluidine, perhaps a mixture of 1:2 and 1:3 iodotoluene?) yields 1:3 iodobenzoic acid.		
1:2 Nitrotoluene (direct from toluene, together with the 1:4 compound; liquid; burns away on oxidation).	1:3 Nitrotoluene (liquid; yields nitrobenzoic acid).	
1:2 Toluidine (liquid; chief constituent of 'pseudotoluidine,' from the nitrotoluene above).	1:3 Toluidine (liquid; from the above nitrotoluene).	1:4 Toluidine (solid; from the above nitrotoluene: ordinary toluidine).

\* The prefixes 'Ortho' and 'Meta' are here used in the sense originally assigned to them by Kekulé. Meyer reverses them, designating the 1:2 derivatives as *meta*, and the 1:3 derivatives as *ortho*. This change, however, appears inadvisable, since it involves the necessity of altering the designation of a large number of compounds—hydroquinone and pyrocatechin among the rest—whose position in the system, nevertheless, remains unchanged; whereas, by retaining the original signification of the prefixes *ortho* and *meta*, all that is necessary is to reverse their application to certain derivatives of benzoic acid, viz. salicylic acid, oxybenzoic acid, and their congeners, which, as Meyer's experiments have shown, must actually be transferred from one series to the other, salicylic acid having been shown to belong to the 1:2, and oxybenzoic acid to the 1:3 series.



*Di-derivatives of Benzene—continued.*

ORTHO SERIES.	META-SERIES.	PARA-SERIES.
1:2	1:3	1:4
1:2 Toluene-sulphonic acid (direct from toluene, together with the 1:4 compound; yields sulcyclic acid).	Isoxylene (yields isophthalic acid).	1:4 Toluene-sulphonic acid (direct from toluene; yields pamoxy-benzoic acid).
1:2 Xylene (yields 1:2 toluic acid, and burns away on further oxidation).	Pyrocatechin	Torexylene (yields 1:4 toluic and terephthalic acid).
Hydroquinone. 1:2 Chlorophenol (direct from phenol).	1:3 Chlorophenol (from the diazo-compound of the volatile nitrophenol).	Resorcin.
1:2 Iodophenol (direct from phenol; yields hydroquinone).	1:3 Bromophenol direct from phenol).	1:4 Monophenol (direct from phenol).
1:2 Nitrophenol (direct from phenol; volatile). See PHENOL.	1:3 Iodophenol (direct, together with the 1:2 compound; yields pyrocatechin).	1:4 Iodophenol (from dinitrobenzene; yields resorcin). ?
1:2 Amidophenol (from the above nitrophenol; yields quinone).	1:3 Nitrophenol (direct from phenol; not volatile).	1:4 Phenolsulphonic acid (from phenol and sulphuric acid at higher temperatures; yields resorcin).
Chloraniline (from acetanilide; probably 1:2).	1:3 Amidophenol (from the above nitrophenol).	1:4 Phenolsulphonic acid (from phenol and sulphuric acid at higher temperatures; yields pyrocatechin).
1:2 Bromaniline (from acetanilide; yields benzidine).	1:3 Phenolsulphonic acid (from phenol and sulphuric acid at ordinary temperatures; yields pyrocatechin).	1:4 Chloraniline (from dinitrobenzene).
1:2 Iodaniline (direct from aniline; yields hydroquinone).	1:3 Bromaniline from $\beta$ -bromonitrobenzene).	1:4 Bromaniline (from dinitrobenzene).
1:2 Nitraniline (from acetanilide).	1:3 Iodophenol (direct, together with the 1:2 compound; yields pyrocatechin).	1:4 Iodaniline (from dinitrobenzene).
1:2 Phenylene-diamine (melts at 140°; from the above nitraniline; yields quinone).	1:3 Amidophenol (from the above nitrophenol).	1:4 Nitraniline (from dinitrobenzene).
Amidobenzene-sulphonic acid (from Schmitt's and Laurent's nitrobenzene-sulphonic acid; constitution unknown).	1:3 Phenylene-diamine (melts at 99°; from isodiamidobenzoic acid).	1:4 Phenylene-diamine (melts at 63°; from dinitrobenzene).
1:2 Bromobenzene sulphonic acid (from benzene-sulphonic acid and bromine; appears to yield hydroquinone).	Sulphanilic acid (from aniline and sulphuric acid; yields resorcin and terephthalic acid).	Sulphanilic acid (from aniline and sulphuric acid; yields resorcin and terephthalic acid).

*Di-derivatives of Benzene—continued.*

ORTHO-SERIES.	META-SERIES.	PARA-SERIES.
1 : 2	1 : 3	1 : 4
Iodobenzenesulphonic acid (constitution unknown).		
Nitrobenzenesulphonic acid (constitution unknown: from nitrobenzene (Schmitt); from benzene-sulphonic acid (Laurent); from benzene-sulphurous acid (Otto and Ostrop).		
<div style="display: flex; justify-content: space-between;"> <div style="width: 33%; border-right: 1px solid black; padding-right: 10px;"> <p style="text-align: center;">Dichlorobenzenes (solid; constitution doubtful).</p> <p>Chlorobromobenzene (perhaps 1 : 2; from the diazo-compounds of 1 : 2 brom- and chlor-aniline).</p> <p>Chloriodobenzene (perhaps 1 : 2; from the diazo-compound of the above chloraniline).</p> <p>1 : 2 Chloronitrobenzene (m. p. 83°; from the diazo-compound of the 1 : 2 nitraniline).</p> </div> <div style="width: 33%; border-right: 1px solid black; padding-right: 10px;"></div> <div style="width: 33%; padding-left: 10px;"> <p>Benzenedisulphonic acid (yields resorcin and terephthalic acid).</p> </div> </div>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 33%; border-right: 1px solid black; padding-right: 10px;"> <p style="text-align: center;">Liquid Dibromobenzenes (constitution unknown. See page 139).</p> <p>Bromiodobenzenes (from 1 : 2 iodaniline).</p> <p>1 : 2 Bromonitrobenzene (m.p. 125°; by nitration of bromobenzene; yields 1 : 2 bromaniline).</p> <p>Di-iodobenzene (m.p. 127°; perhaps 1 : 2).</p> <p>1 : 2 Nitro-iodobenzene (m. p. 171.5°; from iodobenzene and from 1 : 2 nitraniline).</p> </div> <div style="width: 33%; border-right: 1px solid black; padding-right: 10px;"> <p>1 : 3 Bromonitrobenzene (m. p. 37°; Hübner a. Alsberg's <math>\gamma</math>-compound; by nitration of bromobenzene, together with the 1 : 2 compound).</p> </div> <div style="width: 33%; padding-left: 10px;"> <p>1 : 4 Chlorobromobenzene (liquid; from dinitrobenzene).</p> <p>1 : 4 Chloronitrobenzene (m. p. 146°; from dinitrobenzene).</p> <p>1 : 4 Dibromobenzene (solid; yields terephthalic acid. See page 139).</p> <p>1 : 4 Bromonitrobenzene (m. p. 56°; from dinitrobenzene).</p> <p>1 : 4 Di-iodobenzene (m. p. 94°; from dinitrobenzene).</p> <p>1 : 4 Nitro-iodobenzene (m. p. 34°; from dinitrobenzene).</p> <p>Dinitrobenzene (yields resorcin).</p> </div> </div>		

Other classifications of the di-derivatives of benzene have also been proposed. V. v. Richter (*Deut. Chem. Ges. Ber.* iv. 553) places resorcin in the same series as salicylic acid, and pyrocatechin with paraoxybenzoic acid. Peterson (*ibid.* vi. 368) deviates still further from the usual arrangement, placing pyrocatechin with salicylic acid in the 1 : 2 series; resorcin and dinitrobenzene in the 1 : 3 series, and hydroquinone in the 1 : 4 series; and the arguments in favour of this last view appear to have considerable weight. See the article **PHENOLS** in this volume (p. 924).

**Bromobenzenes.**—*Dibromobenzene*,  $C_6H_4Br_2$  (F. Riese, *Ann. Ch. Pharm.* clxiv. 176; Meyer a. Stüber, *Deut. Chem. Ges. Ber.* iv. 956, and v. 52). This compound is known in three isomeric modifications, one solid at ordinary temperatures, the other two liquid. The first [a], which is the ordinary modification (commonly called Couper's), is obtained by the action of bromine on benzene or on monobromobenzene. It is a magnificently crystalline body, melting at 89°.

The second [ $\beta$ ] was obtained by Riese in small quantity, together with the first, by the action of bromine on benzene. It is a colourless, mobile, strongly refracting liquid, miscible in all proportions with ether and benzene, moderately soluble in cold alcohol. When slowly cooled to  $-27^{\circ}$ , it remains liquid, but solidifies immediately on being touched with a glass rod: the solid melts again at  $-1^{\circ}$ . It dissolves readily in cold fuming nitric acid, forming nitro- $\beta$ -dibromobenzene which crystallises in pale yellow needles, melting at  $58^{\circ}$  and boiling at  $296^{\circ}$ .

The third modification was obtained by Meyer & Stüber by treating dibromaniline (prepared from acetanilide) with a nearly saturated alcoholic solution of nitrous acid. Reaction begins in the cold and is completed by warming. The product separated by water is, when purified, a clear colourless liquid, boiling, like the second modification, at  $215^{\circ}$ , but not solidifying even at  $-28^{\circ}$ . It is not perceptibly acted upon by the strongest nitric acid in the cold, but dissolves only on warming, and is converted into a nitrodibromobenzene, which crystallises in pure glistening pale yellow needles, melting at  $60^{\circ}$ - $61^{\circ}$ .

The following is a tabular view of the properties of the three dibromobenzenes:—

Dibromobenzenes	Melting point	Boiling point	Behaviour with $\text{HNO}_3$	Mononitro-derivative
Couper's . . . .	$80^{\circ}$	$219^{\circ}$	Dissolved on warming.	Plates or flat needles, melting at $84^{\circ}$ .
Riese's . . . .	$-1^{\circ}$	$213^{\circ}$ - $215^{\circ}$ (corrected)	Dissolved with spontaneous evolution of heat.	Fine needles, melting at $58^{\circ}$ .
Meyer & Stüber's . (?) * . . . .	Liquid at $-28^{\circ}$	About $215^{\circ}$ (uncorrected)	Dissolved on warming.	Needles, melting at $60^{\circ}$ - $61^{\circ}$ .

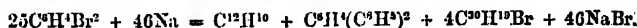
*Action of Sodium on Crystallised Dibromobenzene* (Riese, *Zeitschr. f. Chem.* vi. 735; *Ann. Ch. Pharm.* cxiv. 161). When solid dibromobenzene is added to cold anhydrous ether holding in solution a quantity of sodium twice as great as that which should be required for the complete removal of the bromine, and the mixture is heated in a water-bath, reaction sets in after the heating has been continued for several hours, and then goes on without further application of heat, the mixture continuing to boil gently, until, after 5-7 hours, the sodium is entirely covered with a loose green-black mass. On exhausting the product with ether and mixing the ethereal extract with a considerable quantity of alcohol, a yellow-brown mass separates, and the supernatant liquid, when evaporated, gives a moss-like crystallisation, only a portion of which, however, is re-dissolved by alcohol. By repeating the treatment with alcohol, &c., several times, the product may be separated into two portions, one soluble in alcohol and containing but little bromine, the other insoluble and containing much bromine.

On submitting the mixed product to distillation, diphenyl,  $\text{C}_6\text{H}_5$ , passes over in small quantity as a white crystalline body. The residue, when again distilled, decomposes to a considerable extent, but at the same time yields a crystalline body, which, when purified by repeated distillation, washing with petroleum-naphtha (ligroin), and final recrystallisation from benzene, has the composition of diphenylbenzene,  $\text{C}_{12}\text{H}_{10} = \text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ . The same body is obtained by the action of sodium on a mixture of mono- and dibromobenzene. It melts at  $205^{\circ}$  (corr.), and boils at a temperature above  $400^{\circ}$  (in vapour of boiling sulphur); it is insoluble in alcohol, but dissolves easily in benzene, from which it separates on cooling in small flat white needles. It is scentless in the cold, and smells but faintly when heated; does not volatilise with vapour of water, but sublimates even below its melting point.

The main product of the action of sodium on dibromobenzene is, however, the brown amorphous brominated body above mentioned. This substance is nearly insoluble in alcohol and ether, but dissolves easily in benzene and carbon bisulphide,

\* In Riese's first paper (*Deut. Chem. Ges. Ber.* ii. 60 [1869]), the second modification was said to solidify in a freezing mixture, but he now states that it remains liquid at  $-27^{\circ}$ , unless touched with a solid body. The second and third modifications, therefore, resemble one another in their behaviour at low temperatures, as well as in their boiling points, and differ only in their behaviour with fuming nitric acid, and the melting points of the resulting nitro-derivatives.

from which it is again precipitated in the amorphous state on addition of alcohol or ether. A product thus purified gave by analysis 77.49 p. c. carbon, 4.07 hydrogen and 17.68 bromine, which is nearly the composition of monobromopentaphenylene,  $C^{10}H^{10}Br$  (calc. 78.43 p. c. C., 4.14 H. and 17.43 Br.). The reaction may perhaps be represented by the equation:



**Constitution of Crystallised Dibromobenzene.**—When crystallised dibromobenzene, obtained by the direct action of bromine on benzene, is mixed with methyl iodide and sodium in a flask surrounded by ice, reaction does not begin for several hours, not indeed till the ice is melted; it then proceeds quietly and yields a large quantity of a hydrocarbon, the greater part of which passes over between  $135^{\circ}$  and  $140^{\circ}$ . This hydrocarbon oxidised with potassium chromate and sulphuric acid yields terephthalic acid without any trace of isophthalic acid. This transformation seems to show that crystallised dibromobenzene belongs to the para-series, the two bromine-atoms being separated by two intervals, as represented by the formula  $C^6Br^1H^1Br^3H^3$  (V. Meyer, *Deut. Chem. Ges. Ber.* iii. 753).

On the other hand, V. v. Richter (*ibid.* iv. 459), states that this same dibromobenzene is obtained by acting with phosphorus pentabromide on orthobromophenol, whence it would appear to be itself an ortho-compound,  $C^6Br^1Br^2H^3H^3$ ; and this view is in accordance with the fact that when nitrate of orthobromaniline is heated with nitrous acid and bromine-water, and the nitrate of diazobromobenzene thereby precipitated is decomposed by boiling with alcohol, a dibromobenzene is obtained identical with that which is formed by the direct action of bromine on benzene.

**Chlorobenzenes.** The statements respecting these compounds given in the 1st Suppl. (pp. 264-266), on the authority of Jungfleisch, have been modified in some respects by subsequent experiments of that chemist (*Ann. Ch. Phys.* [4] xv. 186). They are obtained: (1) By the action of iodine chloride on benzene; (2) By distilling with alcoholic potash the mixture of additive compounds produced by the action of chlorine in sunshine on benzene, monochlorobenzene, or sulphobenzide.

1. Chlorine is passed into commercial crystallisable benzene mixed with iodine, the mixture being gently heated at first, after which the action goes on by itself. Monochlorobenzene is first formed, then dichlorobenzene, whereupon the mass solidifies on cooling; on continuing the passage of the chlorine, trichlorobenzene is formed, and the mass again liquefies. At length it becomes solid again, and must be heated more strongly to melt the tetrachlorobenzene which is then formed; and, finally, when pentachlorobenzene has been formed, the product becomes again more fusible. Hexachlorobenzene is not easily obtained by this process, inasmuch as a high temperature is required, at which iodine and chloride of iodine are driven off. In every case, *all* the substitution-products are formed simultaneously, but *one* of them always predominates, according to the temperature and other circumstances of the reaction. The mixture likewise contains small quantities of iodobenzenes; but by exposing the product to sunshine, or by distillation, these compounds are decomposed, with liberation of iodine, which may then be removed by potash.

2. The oily liquid formed, together with crystals of the compound  $C^6H^5Cl$ , by the action of excess of chlorine in sunshine on monochlorobenzene, is separated from the crystals and gently warmed with alcoholic potash, and the resulting brown liquid is treated with water, which throws down a mixture of an oil with crystals, while chlorinated phenols and other products remain in solution. The mixture of oil and crystals yields by fractional distillation a series of chlorinated benzenes.

The monochlorobenzenes obtained by the two processes are the same: but the di-, tri-, tetra- and penta(?)-chlorinated compounds obtained by the second process are different from those produced by the first. It will be convenient to distinguish these modifications by the symbols  $\alpha$  and  $\beta$ .

**Monochlorobenzene**,  $C^6H^5Cl$ , prepared as already described (1st Suppl. 265), and finally purified by cooling to  $-35^{\circ}$ , and filtering at that temperature, boils constantly at  $131^{\circ}$ , and solidifies between  $-50^{\circ}$  and  $-60^{\circ}$  to a hard crystalline mass, which melts at  $-40^{\circ}$ . Its specific gravity is 1.1293 at  $0^{\circ}$ ; coefficient of expansion 0.00116. Its physical properties are therefore identical with those of phenyl chloride obtained by the action of phosphorus pentachloride on phenol. It is not attacked by potassium hydrate, or at ordinary temperatures by potassium; when heated with sodium it yields diphenyl; this latter compound is also formed, together with other products, when the vapour of chlorobenzene is passed over red-hot copper.

$\alpha$ -Dichlorobenzene,  $C^6H^4Cl^2$ , forms colourless transparent crystals belonging to the monoclinic system (not orthorhombic, as formerly stated); plane angle of the

rhombic base =  $43^{\circ}17'56''$ ; inclination of principal axis to this face =  $46^{\circ}30'$  (Descloizeaux). It melts at  $53^{\circ}$ , and boils without decomposition at  $171^{\circ}$ .

Specific gravity	1.4581	1.241	1.2062	1.1366
at	20.5°	63°	93°	161°

Strong sulphuric acid does not act upon it in the cold, but under the prolonged influence of heat unites with it, forming a sulpho-acid.

$\beta$ -Dichlorobenzene melts below  $0^{\circ}$ , and boils at about  $175^{\circ}$ .

$\alpha$ -Trichlorobenzene,  $C_6H_3Cl_3$ , is difficult to prepare by the method above described, and can be obtained only from perfectly pure benzene. It is best prepared by passing chlorine into purified dichlorobenzene mixed with iodine, separating from time to time the still liquid portion from the crystals, and treating the latter further with chlorine. The product, after washing with water and sodium carbonate, is subjected to fractional distillation, and the higher and lower chlorobenzenes, which crystallise more readily, are separated by cooling the distillate. By further fractional distillation a product boiling at  $206^{\circ}$  is obtained, which is to be cooled with ice water, and brought in contact with a crystalline fragment obtained by cooling the liquid in a freezing mixture. The liquid in the ice-water then gradually solidifies into crystals, which may be freed from the still fluid portion by decantation. By repetition of this process the portion which still remains fluid may be reduced to a very small amount.

Trichlorobenzene thus prepared, forms large, transparent and colourless crystals, apparently belonging to the rhombic system; it melts at  $17^{\circ}$ , boils at  $206^{\circ}$ , and has a rather strong but not unpleasant odour:—

Sp. gr.	1.5740 (cryst.)	1.4658 (liq.)	1.4460	1.4111	1.2427
at	10°	10°	26°	56°	196°

whence the expansion coefficient for the liquid state is 0.000989. A mixture of this compound with  $\alpha$ -dichlorobenzene, in equal numbers of molecules, may be cooled to  $10^{\circ}$ , without formation of crystals; but towards  $0^{\circ}$  part of the dichlorobenzene separates out, and below  $0^{\circ}$  the whole solidifies.  $\alpha$ -Trichlorobenzene dissolves in alcohol ether, carbon sulphide and benzene. It is a very stable compound, not being acted on by aqueous potash or decomposed by distillation over caustic baryta, or deprived of any portion of its chlorine by strong heating with alcoholic potash. Heated with strong sulphuric acid nearly to the boiling point, it forms trichlorobenzene-sulphonic acid,  $C_6H_3Cl_3SO_3$ , which crystallises at ordinary temperatures, and may be precipitated from the sulphuric acid solution by addition of water. Pure trichlorobenzene is converted by fuming nitric acid, with evolution of heat, into nitro-trichlorobenzene, but in the impure state it is but slowly acted on, the nitration taking place only after prolonged boiling.

$\beta$ -Trichlorobenzene, formed together with the  $\alpha$ -modification by the second process above described, melts at  $60^{\circ}$ .

The more highly chlorinated derivatives of benzene are, for the most part, sufficiently described in the *First Supplement*.

$\alpha$ -Tetrachlorobenzene melts at  $139^{\circ}$ , boils at  $210^{\circ}$ , and exhibits the following specific gravities:—

Sp. gr.	1.7344	1.4339	1.3958	1.3281
at	10°	149°	170°	230°

$\beta$ -Tetrachlorobenzene melts at  $35^{\circ}$ , and boils at  $253^{\circ}$ .

Of pentachlorobenzene there should, according to Kekulé's theory, be only one modification, but Jungfleisch and Otto assert that there are two; both of which are found amongst the products of the action of alcoholic potash on the additive compounds obtained by the action of chlorine on monochlorobenzene or on sulphobenzide in sunshine, and may be separated by boiling alcohol, in which one is soluble, the other insoluble; one of them ( $\alpha$ ) is also the most abundant of the products formed by the action of chlorine and iodine on benzene. The  $\alpha$ -modification melts at  $74^{\circ}$ , and boils at  $272^{\circ}$ ; the  $\beta$ -modification (insoluble in boiling alcohol) forms shining, silky needles, which melt at  $175^{\circ}$  when quickly heated, but after solidification from fusion do not melt again till heated to  $198^{\circ}$ , and resolidify at a slightly lower temperature. The  $\alpha$ -modification exhibits the following specific gravities:—

Sp. gr.	1.8422	1.8342	1.6691 (fused)	1.5732	1.3824
at	10°	16.5°	84°	114°	261°

Ladenburg (*Deut. Chem. Ges. Ber. v. 789*) is of opinion that the existence of the second modification of pentachlorobenzene (melting at  $175^{\circ}$ – $198^{\circ}$ ) is by no means satisfactorily proved. On repeating Jungfleisch's mode of preparation, that is to say,

exposing monochlorobenzene to the action of chlorine in sunshine (using, however, moist instead of dry chlorine), distilling the product with alcoholic potash, subjecting the distillate to repeated fractional distillation, and the several fractions to fractional crystallisation from alcohol, till the melting and boiling points of the several portions became nearly constant, he finally obtained the following compounds, and no others:—

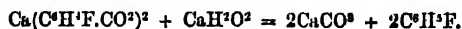
$\text{C}^6\text{H}^5\text{Cl}^4$	melting at $27^\circ\text{--}28^\circ$ ,	boiling at $245^\circ\text{--}248^\circ$
$\text{C}^6\text{HCl}^5$	" $85^\circ\text{--}86^\circ$	" $275^\circ\text{--}277^\circ$
$\text{C}^6\text{Cl}^6$	" $225^\circ$	

From these results Ladenburg concludes that by the action of moist chlorine on monochlorobenzene in sunshine only one pentachlorobenzene is produced (that designated above as a): and, considering that the statements of Jungfleisch and Otto with respect to the properties of the second modification do not quite agree; that, according to Jungfleisch, the melting point of this supposed modification varies from  $175^\circ$  to  $198^\circ$ , and that among the products of the action of moist chlorine on benzene, this particular product is not found, whereas all the others products obtained by the action of dry chlorine do likewise occur in this case; he concludes that the existence of this second modification of pentachlorobenzene must be regarded as doubtful until it is established by new and decisive experiments.

Jungfleisch (*Bull. Soc. Chim.* [2] xviii. 531) replies to these observations, maintaining the existence of the second modification of pentachlorobenzene described by himself and by Otto, and attributing Ladenburg's failure in obtaining it to the fact of his having used moist instead of dry chlorine. He states his intention of publishing further results relating to the second pentachlorobenzene and its derivatives.

Otto (*Ann. Ch. Pharm.* cliv. 182) likewise maintains the existence of two modifications of pentachlorobenzene. When dry sulphobenzene is subjected to the prolonged action of chlorine in sunshine, the product dissolved in alcohol (which leaves undissolved small quantities of dichlorobenzene chloride), decomposed by potash, and water then added, the two pentachlorobenzenes are thrown down, and may be separated by alcohol, in which the less fusible of the two is insoluble. The more fusible modification melts at  $85^\circ$ , the less fusible at  $198^\circ\text{--}199^\circ$ . These statements do not agree very well with those of Jungfleisch. Moreover, Ladenburg, by the analysis of two samples of so-called pentachlorobenzene prepared by Otto, one melting at  $224^\circ\text{--}225^\circ$ , the other at  $219^\circ\text{--}223^\circ$ , found that they contained respectively 74.39 and 74.06 p.c. chlorine, from which it appears that they were both nearly pure hexachlorobenzene, which melts at  $226^\circ$ , and contains 74.74 p.c. chlorine.

**Fluobenzene**,  $\text{C}^6\text{H}^5\text{F}$ , is obtained by heating the calcium salt of fluobenzonic acid with about four times its weight of slaked lime:



The fluobenzene, after being purified by fractional distillation, solidifies to a mass of scales. It melts at  $40^\circ$ , boils at  $180^\circ\text{--}183^\circ$ , and has a vapour-density of 3.476 (calc. 3.937). It is insoluble in water, but dissolves easily in ether and in alcohol; smells like benzene, and burns with a smoky flame (Schmitt u. Gehron, *J. pr. Chem.* [2] i. 394).

**Nitrobenzenes.** *Mononitrobenzene*,  $\text{C}^6\text{H}^5\text{NO}^2$ , is but slowly attacked by *chromic oxychloride* mixed with glacial acetic acid. Nitrotrichlorobenzonic acid is probably formed, together with an unknown substance, which strongly attacks the eyes (Carstanjen, *J. pr. Chem.* [2] ii. 83).

Nitrobenzene, heated with *potassium* or *sodium hydrate*, gives off ammonia and aniline, and on pouring the product into dilute hydrochloric acid, a brown tarry matter separates, which solidifies to a crystalline mass of azobenzene. These, however, are only the final products of the reaction; for if it be stopped at a certain stage, the product dissolves almost completely in water, and hydrochloric acid added to the solution throws down dark flocks of a resinous acid (Morz u. Coray, *Dent. Chem. Ges. Ber.* iv. 981).

According to Post u. Hübner (*ibid.* v. 408) nitrobenzene brought in contact for a short time with potassium hydrate heated to fusion, gives off hydrocyanic acid; dinitrobenzene is acted upon in a similar manner when boiled with solution of caustic potash or soda.

**Nitrobenzobenzene**,  $\text{C}^6\text{H}^5\text{Br}(\text{NO}^2)$ . Three modifications of this compound are known, viz. 1.—1. *Ortho-* or  *$\alpha$ -Nitrobromobenzene* (1: 2), produced by the action of fuming nitric acid on monobromobenzene, also, according to Griess, by heating the bromoplatinate of  *$\alpha$ -azophenylamine* (from  *$\alpha$ -nitraniline*) with sodium carbonate (*ibid.* 416).

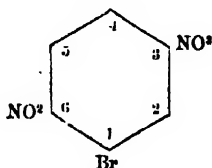
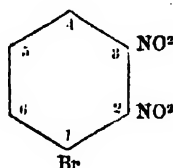
It melts at  $125^{\circ}$ – $126^{\circ}$ , crystallises in long white needles, and is converted by ammonium sulphide or ferrous acetate into  $\alpha$ -bromaniline melting at  $64^{\circ}5'$ .

2. *Meta- or  $\beta$ -Nitrobromobenzene* crystallises from the mother-liquor of the preceding compound in long needles, melting at  $37^{\circ}$ , and boiling almost without decomposition at  $250^{\circ}$ – $251^{\circ}$ . Its formation is most favoured by effecting the nitration at a temperature of  $90^{\circ}$ – $95^{\circ}$ . By reduction with tin and hydrochloric acid it yields  $\beta$ -bromanilino, which when precipitated with soda-ley and distilled with water, passes over as an oil, solidifying in a freezing mixture to crystals, and when quickly pressed and dissolved in alcohol separates therefrom in white needles melting at  $31^{\circ}$  (Hübner a. Alsberg, *Zeitschr. f. Chem.* [2] vi. 369).

*Para- or  $\gamma$ -Nitrobromobenzene\** is the modification which Griess obtained by heating the perbromide of  $\beta$ -azonitrophenyl ammonium with sodium carbonate (iv. 416). It melts at  $56^{\circ}$ , and is reduced by ammonium sulphide to parabromaniline (Griess, iv. 426, 435).

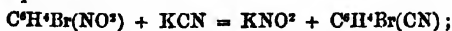
The three modifications of nitrobromobenzene yield corresponding nitranilines when heated to  $180^{\circ}$ – $190^{\circ}$  in sealed tubes with strong alcoholic ammonia. Ortho-nitraniline thus produced melts at  $146^{\circ}$ , and agrees in every respect with that obtained from acetanilide; meta-nitraniline, recently discovered by Walker a. Zincke, (*Deut. Chem. Ges. Ber.* v. 114), melts at  $66^{\circ}$ ; paranitraniline, originally obtained by reduction of dinitrobenzene (iv. 445), at  $108^{\circ}$ .

Ortho- and meta-nitrobromobenzene, when subjected to the further action of fuming nitric acid, yield one and the same dinitro-bromobenzene,  $C^6H^3Br(NO^2)_2$ , melting at  $72^{\circ}$  (Walker a. Zincke). Now, assuming that the bromine and nitryl in these two modifications occupy the positions 1 : 2 and 1 : 3, it is easily seen that dinitrobromobenzene must be either 1 : 2 : 3 or 1 : 3 : 6, as represented below:—

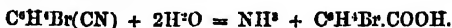


To decide which of these is the actual arrangement, the dinitro-bromobenzene was heated with tin and hydrochloric acid, whereby the two groups  $NO^2$  were replaced by  $H^2$ , and at the same time bromine by hydrogen, the result being paraphenylenediamine,  $C^6H_4(NH^2)_2$ , identical with that obtained from dinitrobenzene. This shows that in the dinitro-bromobenzene the two groups  $NO^2$  must be separated by two intervals, and consequently that the bromine and these two nitryls must occupy positions 1 : 3 : 6 (Zincke a. Sintonis, *Deut. Chem. Ges. Ber.* v. 791).

Ortho- and para-nitrobromobenzene heated with pure potassium cyanide and alcohol  $180^{\circ}$ – $200^{\circ}$ , yields cyano-bromobenzene, together with potassium nitrite, according to the equation:



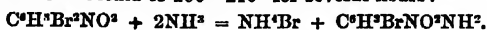
by boiling the product with alcoholic potash as long as ammonia is given off, then distilling with water, filtering, and adding hydrochloric acid, a precipitate is obtained, consisting of bromobenzoic acid:



*Dinitrobromobenzene*,  $C^6H^3Br(NO^2)_2$ . The formation of the dinitrobromobenzene melting at  $72^{\circ}$  by the action of fuming nitric and sulphuric acid on monobromobenzene (1st Suppl. 269) appears, from the observations of Clemm (*J. pr. Chem.* i. 145), to be accompanied by that of another modification melting at a lower temperature. Dinitrobromobenzene melting at  $72^{\circ}$  heated with strong potash-ley is dinitrophenol,  $C^6H^3(NO^2)_2(OH)$ , melting at  $113^{\circ}$ – $114^{\circ}$ ; and when heated in alcoholic ammonia, dinitranilino,  $C^6H^3(NO^2)_2.NH^2$ .—Aniline heated with nitrobromobenzene acts violently on its forming dinitrodiphenylamine identical with that obtained by Hofmann (Clemm).

\*There is some confusion about the designation of these isomerides. Hübner a. Alsberg, who described the second modification above described, distinguished it by the prefix  $\beta$ , but Walker a. Zincke (*Deut. Chem. Ges. Ber.* v. 114) designated it as  $\gamma$ , and the para-modification as  $\beta$ : it is better to adopt the mode of distinction adopted by the discoverers.

**Nitramidobromobenzene**,  $C^6H^3Br(NO^2)(NH^2)$ , is produced by heating nitrodibromobenzene (prepared by boiling solid dibromobenzene with fuming nitric acid) with concentrated alcoholic ammonia to  $200^{\circ}$ – $210^{\circ}$  for several hours:



On pouring the black liquid into hydrochloric acid, separating the red-brown solution thereby formed from resin, and pouring it into water, nitramidobromobenzene separates in fine felted orange-coloured needles, which may be purified by crystallisation from ether, repeated solution in hydrochloric acid, and reprecipitation by water.

Nitramidobromobenzene melts at  $104.5^{\circ}$ , sublimes without decomposition, and volatilises readily with vapour of water. It is freely soluble in alcohol and ether, slightly soluble in cold water, somewhat more so in hot water, forming a yellow solution. It has no basic properties, but dissolves in strong hydrochloric or nitric acid, and is reprecipitated on addition of water. Its hot aqueous solution dyes silk and wool of a fine yellow colour. It is not deprived of its bromine even by prolonged digestion with alcoholic ammonia at a very high temperature.

If solid dibromobenzene be a para-compound (p. 136), the mononitro-compound formed from it will probably have the constitution 1 : 2 : 4; and the amido-compound formed from this by substitution of  $NH^2$  for Br, will be similarly formed, thus:—

		1	2	3	4	5	6
Paradibromobenzene . . . .	$C^6$	Br	H	H	Br	H	H
Nitrodibromobenzene . . . .	$C^6$	Br	$NO^2$	H	Br	H	H
Nitramidobromobenzene . . . .	$C^6$	$NH^2$	$NO^2$	H	Br	H	H
or . . . . .	$C^6$	Br	$NO^2$	H	$NH^2$	H	H

By treating this last compound with tin and hydrochloric acid, the  $NO^2$  is replaced by  $NH^2$ , and a bromophenylene-diamine,  $C^6H^3Br(NH^2)^2$ , is obtained having the two amide groups either in close proximity (1 : 2), or separated by one interval (2 : 4 or 1 : 3). On adding excess of soda, agitating the product with ether, and evaporating the ethereal solution, the bromophenylene-diamine is obtained as a thick liquid, which solidifies over sulphuric acid to a reddish crystalline mass. By heating it with water and sodium-amalgam, the bromine is replaced by hydrogen, and phenylene-diamine,  $C^6H^4(NH^2)^2$ , is formed, likewise having the two amide groups disposed either as 1 : 2 or as 1 : 3; that is to say, it is either ortho- or meta-phenylene-diamine. (In Meyer's table, p. 137, the latter position is assigned to it). This phenylene-diamine melts at  $99^{\circ}$ , and is identical in characters and reactions with that which Griess obtained by the dry distillation of  $\beta$ -diamidobenzoic acid (Meyer a. Wurster, *Deut. Chem. Ges. Ber.* vi. 362). See PHENYLENE-DIAMINES.

**Nitrochlorobenzenes** (Jungfleisch, *Ann. Chim. Phys.* [4] xv. 186; Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* [2] vi. 225; Clemm, *ibid.* 444).—**Nitromonochlorobenzene**,  $C^6H^4(NO^2)Cl$ , is known in two modifications, both of which are formed when monochlorobenzene is poured into cool fuming nitric acid; they are separated by their difference of solubility in cold alcohol. The modification designated as *a*, which is but slightly soluble in this liquid, forms long crystalline laminae, derived from a rhombic prism of about  $125^{\circ}30'$ ; melts at  $83^{\circ}$ ; and has, after solidification, a specific gravity of 1.380 at  $22^{\circ}$ : it boils without decomposition at  $242^{\circ}$  (bar. at 761 mm.); smells like bitter almonds and Tonka beans. Ether, benzene, carbon sulphide, boiling alcohol, and hot nitric acid dissolve it readily. It is not attacked by aqueous potash, but *alcoholic potash* acts strongly upon it, probably forming chlorinated azoxybenzene. Strong sulphuric acid dissolves it easily and turns brown-red when boiled with it, giving off a large quantity of sulphurous oxide; at comparatively low temperatures, the product consists of nitrochlorobenzene-sulphonic acid. *Fuming nitric acid* does not act upon it, but a mixture of strong nitric and sulphuric acids quickly converts it into *a*-dinitro-chlorobenzene. By *tin and hydrochloric acid* the mononitrated compound is reduced to monochloraniline,  $C^6H^4ClN$ , which appears to be identical with that which Hofmann obtained from chlorisatin.

**$\beta$ -Nitromonochlorobenzene**, the modification which dissolves easily in cold alcohol, is purified by filtration in a small quantity of very cold alcohol and precipitated with water. It solidifies in a freezing mixture. When placed in ice-water and mixed with a few fragments of the portion which has previously solidified in the crystalline form, it crystallises and may be freed from the still liquid portion by decantation. By repeatedly subjecting the crystallised portion to the same treatment, that is, dissolving it in a small quantity of cold alcohol and causing it to solidify by touching it after cooling with a crystal of the same modification, it is finally obtained in tufts of beautiful needle-shaped crystals, having a nacreous lustre, a scarcely perceptible yellowish tinge, and a fragrant odour like that of Tonka beans or clover. It melts at  $15^{\circ}$ , boils at about  $243^{\circ}$ , and has a density of 1.368 at  $22^{\circ}$ . In the fused



state it is miscible with alcohol in all proportions; ether, carbon sulphide, benzene and dilute nitric acid dissolve it readily. With potassium hydrate it reacts like the first modification. Fuming nitric acid acts easily upon it, especially at the boiling heat, converting it into  $\alpha$ - and  $\beta$ -dinitromonochlorobenzene. A mixture of nitric and sulphuric acids acts upon it explosively. With strong sulphuric acid it behaves like the  $\alpha$ -modification. By *tin* and *hydrochloric acid* it is easily reduced to  $\beta$ -monochloraniline, which is obtained as a liquid not solidifying at low temperatures.

*$\alpha$ -Dinitromonochlorobenzene*,  $C^6H^4(NO^2)_2Cl$ , is easily prepared from  $\alpha$ - or  $\beta$ -mononitrochlorobenzene, or directly from monochlorobenzene, by the action of a warm mixture of strong nitric and sulphuric acids, and precipitation with water; it may be purified by several recrystallisations from alcohol, or better from boiling ether (Jungfleisch). It is also produced by the action of phosphorus pentachloride on dinitrophenol (Clemm). It forms large, transparent, very faintly yellowish crystals, which, according to Descloizeaux, are orthorhombic prisms of  $102^{\circ}5'$ . It has a faint odour at ordinary temperatures, but, when heated, gives off very irritating vapours. It has a density of 1.697 at  $22^{\circ}$ , melts at  $50^{\circ}$ , and boils with slight decomposition at  $315^{\circ}$ . It is insoluble in water, and very slightly soluble in cold alcohol, but boiling alcohol, as well as ether, benzene, and carbon sulphide dissolve it freely. *Fuming nitric acid* likewise dissolves it without decomposition. Strong *sulphuric acid* unites with it when heated, forming a sulfo-acid. By *alcoholic potash* it is attacked in the same manner as nitrobenzene. *Tin* and *hydrochloric acid* convert it into nitrochloraniline, which is obtained in fine orthorhombic crystals, melting at  $89^{\circ}$ , and decomposing partially when volatilised (Jungfleisch).

By strong *aqueous potash*, or by *alcoholic soda-solution*, it is converted into dinitrophenol. Heated for four or five hours to  $100^{\circ}$ – $120^{\circ}$  with *alcoholic ammonia*, it yields  $\alpha$ -dinitraniline,  $C^6H^3(NO^2)_2NH^2$ , which crystallises in light yellow prisms, melting at  $175^{\circ}$  (Clemm).

*$\beta$ -Dinitrochlorobenzene* is obtained with difficulty from mononitrochlorobenzene by heating with nitric acid; it is precipitated with water, washed with water and then with boiling alcohol, and recrystallised from solution in cold ether. According to Descloizeaux' measurements, its crystalline form is similar to, but not identical with that of the  $\alpha$ -modification. The primary form is a right rhombic prism of  $100^{\circ}18'$ . The crystals are faintly yellowish, very brittle, have a density of 1.6867 at  $16^{\circ}5$ , and melt at  $43^{\circ}$ ; the boiling point is about  $315^{\circ}$  (bar. at 0.762 met.). It is scarcely soluble in cold alcohol, more freely in boiling alcohol; ether, benzene, and carbon sulphide dissolve it more readily than the  $\alpha$ -modification. With nitric acid and alcoholic potash it reacts like the latter. By reduction with *tin* and *hydrochloric acid*, it yields  $\beta$ -monochloronitraniline, which crystallises in right rhombic prisms of  $10^{\circ}22'$ .

$\beta$ -Dinitrochlorobenzene undergoes a remarkable change when touched with the smallest fragment of a crystal of the  $\alpha$ -modification, the transparent crystals becoming turbid and passing into the  $\alpha$ -modification; by subsequent crystallisation from ether or carbon sulphide, they are obtained in the exact form of the  $\alpha$ -modification, exhibiting also the same melting point and the same degree of solubility.

On the other hand, the  $\alpha$ -modification may be converted, though less easily, into the  $\beta$ -modification: namely, by suddenly plunging it, while in the fused state, into a freezing mixture, whereupon it solidifies to a homogeneous translucent crystalline mass. Jungfleisch supposes that the substance thus obtained is the  $\beta$ -modification, because it is more fusible than the original  $\alpha$ -modification, and because, when touched with a crystal of the latter, it is gradually converted, from the point of contact inwards, into a turbid crystalline mass, made up of crystals of the more stable  $\alpha$ -modification. These remarkable changes appear, however, to require further examination.

*Nitrodichlorobenzene*,  $C^6H^3(NO^2)Cl_2$ , is prepared by the action of nitric acid of sp. gr. 1.49 on dichlorobenzene (melting at  $53^{\circ}$ ), and purified by precipitation with water and crystallisation from boiling alcohol. From solution in carbon sulphide it separates by spontaneous evaporation in faintly yellow, soft, flexible crystals of the triclinic system. It melts at  $54.5^{\circ}$  and boils at  $266^{\circ}$ . Sp. gr. 1.669 at  $22^{\circ}$ . Boiling alcohol, carbon sulphide, benzene and chloroform dissolve it freely, cold alcohol sparingly. Aqueous potash does not act upon it; alcoholic potash attacks it strongly, probably forming dichlorazoxybenzene. Strong sulphuric acid dissolves it readily, forming a sulfo-acid; in boiling the liquid, sulphurous oxide is given off. By *tin* and *hydrochloric acid*, it is converted into dichloraniline.

*Dinitro-dichlorobenzene*,  $C^6H^2(NO^2)_2Cl_2$ , is formed in two modifications by boiling the preceding compound for an hour with a mixture of fuming nitric and

strong sulphuric acids. One of these, distinguished as the  $\alpha$ -modification, is less soluble in alcohol than the other, and may therefore be obtained pure by crystallisation from alcohol, and washing with the same liquid. It forms small nacreous laminae, having a slight yellowish tint; smells faintly at ordinary temperatures, but gives off a pungent intolerable odour when heated; melts at  $87^\circ$  (at  $104^\circ$ , according to Engelhardt n. Latschinoff); boils with slight decomposition at  $312^\circ$ . After fusion and solidification, it has a specific gravity of 1.103 at  $16^\circ$ . It is nearly insoluble in cold alcohol, but dissolves more easily in boiling alcohol, and still more in ether, carbon sulphide, and benzene. Strong sulphuric acid unites with it, forming a sulpho-acid whose barium salt crystallises easily. Alcoholic potash decomposes it readily, forming crystallised products. Tin and hydrochloric acid convert it into dichloro-nitraniline (Jungfleisch).

Boiled with sodium carbonate, it yields a sodium salt,  $C^6H^2Na(NO^2)^2ClO + 3H^2O$ , which, when decomposed by acids, yields a dinitrochlorophenol,  $C^6H^2(NO^2)^2ClO$ , melting at  $80^\circ$ , and probably identical with that obtained by Dubois and by Faust a. Saamo (1st Suppl. 914). (Engelhardt n. Latschinoff.)

The  $\beta$ -modification of dinitrodichlorobenzene is obtained by evaporation from the mother-liquors of the  $\alpha$ -modification, and may be completely freed from the latter by cooling the hot alcoholic solution of the residue, the  $\beta$ -modification then separating in the crystalline form, while the  $\alpha$ -modification separates as an oil which may be decanted from the crystals together with mother-liquor. The final purification is effected by repeated crystallisation from alcohol. It forms nearly colourless well-defined crystals, melts at  $107^\circ$  (at  $101^\circ$ , according to Engelhardt a. Latschinoff); boils with slight decomposition at  $318^\circ$ , dissolves somewhat more easily than the  $\alpha$ -modification in cold alcohol; but in other solvents the two modifications dissolve with equal facility: they also react in the same manner with sulphuric acid, with alcoholic potash, and with tin and hydrochloric acid (Jungfleisch).—By boiling with sodium carbonate, it is converted into the easily soluble sodium salt of a dinitrochlorophenol, whose barium salt,  $[C^6H^2(NO^2)^2ClO]^2Ba + 3H^2O$ , crystallises in yellow needles. The dinitrochlorophenol separated from it crystallises from water in tufts of long needles, melting at  $70^\circ$  (Engelhardt n. Latschinoff).

*Nitrotrichlorobenzene*,  $C^6H^2(NO^2)Cl^3$ , which Lesimple obtained by the action of fuming nitric acid at the boiling heat on trichlorobenzene (1st Suppl. 269), crystallises from carbon sulphide in light sulphur-yellow, oblique rhombic prisms of  $105^\circ 30'$ , whose prismatic faces make an angle of  $63^\circ 40'$  with the base. It melts at  $75^\circ$  to a yellow liquid, which boils without essential decomposition at  $288^\circ$ . Sp. gr. 1.790 at  $22^\circ$ . It dissolves slightly in cold, more freely in hot alcohol, and with great facility in ether, benzene, and carbon sulphide. Alcoholic potash-ley acts strongly on it; strong sulphuric acid does not act upon it in the cold, but dissolves it when heated, with formation of a sulpho-acid: at the boiling heat the liquid becomes dark, and gives off sulphurous oxide. By tin and hydrochloric acid it is converted into trichloroaniline (Jungfleisch).

*Dinitrotrichlorobenzene*,  $C^6H(NO^2)^2Cl^3$ , is obtained by boiling the preceding compound for some hours with a mixture of strong nitric and sulphuric acids, precipitating with water, washing with dilute potash-ley, and crystallisation from alcohol. It forms light yellow, six-sided, needle-shaped prisms, having a density of 1.850 at  $26^\circ$ ; melts at  $103.5^\circ$ , and boils with slight decomposition at  $335^\circ$ . It is insoluble in cold, but soluble in warm alcohol, also in benzene, carbon sulphide, and ether. Alcoholic potash attacks it with violence; tin and hydrochloric acid convert it into nitrochloroaniline (Jungfleisch).

*Trinitrochlorobenzene*,  $C^6H(NO^2)^3Cl$ , is produced by the action of phosphorus pentachloride on picric acid. It was originally obtained by Pisani (1st Suppl. 416), who, however, does not appear to have prepared it in the pure state. Clemm (Zeitschr. f. Chem. vi. 444) mixes 100 grams of dry picric acid with twice its weight of phosphorus pentachloride in a capacious vessel provided with a wide condensing tube, applying a gentle heat at first, and when the first violent reaction is over, heating the mixture for some time to the boiling point; the greater part of the resulting phosphorus oxychloride is then distilled off, the residue decomposed by water, and the separated trinitrochlorobenzene is washed with a little ether and crystallised from alcohol or light petroleum oil. It crystallises in nearly colourless shining needles, which become dull in contact with the air; melts at  $83^\circ$ , often remaining liquid for a long time. It is not decomposed by boiling water, but solution of sodium carbonate or caustic alkalis decompose it at the boiling heat, forming metallic chloride and trinitrophenol. By ammonia or ammonium carbonate it is converted into trinitroaniline (Pisani's picramide). Aniline acts violently on it, forming trinitrodiphenylamine,  $NH(C^6H^4)[C^6H^2(NO^2)^3]$ . With ethyl aniline, nothing but resinous products are formed. With an alcoholic solution of sodium phenate, trinitrochloro-

benzene yields hydrochloric acid, sodium pierate, and phenol. With an alcoholic solution of *potassium sulphocyanate*, a complicated reaction takes place, yielding a crystallisable body, whose composition has not yet been determined (Clemm).

*Nitrotetrachlorobenzene*,  $C^6H(NO^2)Cl^4$ , is prepared by treating tetrachlorobenzene with strong nitric acid, or better with a mixture of nitric and sulphuric acids. It crystallises from boiling alcohol in thick striated needles; from carbon sulphide by slow evaporation in large transparent and colourless triclinic crystals. It has a peculiar slightly pungent odour; melts at  $99^\circ$ , and boils with decomposition at  $304^\circ$ . Sp. gr. 1.744 at  $25^\circ$ . Insoluble in cold, easily soluble in hot alcohol, also in benzene, carbon sulphide, and chloroform, slightly in hot strong sulphuric acid. By *tin* and *hydrochloric acid*, it is converted into tetrachloraniline (Jungfleisch).

*Nitropentachlorobenzene*,  $C^6(NO^2)Cl^5$ , is formed by the action of fuming nitric acid on pentachlorobenzene (melting at  $74^\circ$ ), and separates from the solution on cooling in beautiful six-sided crystalline plates; after washing with water, and boiling with dilute potash, which removes a quantity of adhering brown substance, it recrystallises from alcohol in slender colourless shining needles, from carbon sulphide in large monoclinic tables; melts at  $146^\circ$ , and boils with partial decomposition at  $328^\circ$ . Sp. gr. 1.718 at  $25^\circ$ . Insoluble in cold alcohol, easily in boiling alcohol, especially when mixed with benzene, still more in carbon sulphide and in chloroform. By *tin* and *hydrochloric acid* it is converted into pentachloraniline,  $C^6Cl^5NH^2$  (Jungfleisch).

In all the nitrochlorobenzenes, the chlorine has completely lost the passive character which it exhibits in the chlorobenzenes, and is replaceable by other radicals, with greater facility in proportion as the compound contains a larger number of nitryl groups.

$\alpha$ - and  $\beta$ -*Nitrochlorobenzene*,  $C^6H(NO^2)Cl$ , heated to  $130^\circ$  for three days with solution of sodium carbonate or hydrate give up their chlorine and are converted into nitrophenols, the  $\alpha$ -modification (melting at  $83^\circ$ ) giving non-volatile nitrophenol, but only in very small quantity, the  $\beta$ -modification yields volatile nitrophenols. Ammonia likewise withdraws the chlorine from these compounds.

*Nitrodichlorobenzene*,  $C^6H^2(NO^2)Cl^2$ , is but little acted upon by caustic soda or by ammonia; but *dinitrochlorobenzene*,  $C^6H(NO^2)^2Cl$ , easily gives up its chlorine, yielding, when boiled with solution of sodium carbonate, a dinitrophenol melting at  $114^\circ$ ; with ammonia, a dinitraniline melting at  $177^\circ$ ; and with toluidine, a compound which melts at  $135^\circ$ , crystallises from ether in long red plates or orange-yellow tables, and probably consists of dinitrophenyl-toluidine,  $C^6H^2(NO^2)^2C^6H^3NH$ . Still more easy is the decomposition of *trinitrochlorobenzene*,  $C^6H^3(NO^2)^3Cl$ , and of *dinitro-dichlorobenzene*,  $C^6H^2(NO^2)^2Cl^2$ ; by boiling with alkalis (pp. 145, 146); the former being converted by ammonia or ammonium carbonate into trinitraniline, the latter by sodium carbonate into dinitromonochlorophenol,  $C^6H^2(NO^2)^2ClO$  (Engelhardt & Latschinoff).

#### Compounds formed by Reduction of the Nitrobenzenes.

**Amidobenzene**,  $C^6H^5(NH^2)$ . See ANILINE under PHENYLAMINES.

*Triamidobenzene*,  $C^6H^3N^3 + C^6H^4(NH^2)^3$ , is obtained by distilling triamidobenzoic acid with pounded glass. It is a crystalline solid, varying in colour between flesh-colour and chocolate. It is readily soluble in water, alcohol, and ether, and remains on evaporation as a radiate crystalline mass, melting at about  $103^\circ$ , distilling at  $336^\circ$  (corrected), and readily subliming at a much lower temperature. The aqueous solution has a strong alkaline reaction, and gives with ferric chloride, first a violet and then a brown precipitate, and with hypochlorites and nitrites brown precipitates. It reduces an ammoniacal silver-solution in the cold. On dissolving triamidobenzene in concentrated sulphuric acid and adding a trace of nitric acid, the liquid assumes at first a dirty green colour, which soon changes into a fine blue and disappears on standing or on dilution with water. The same reaction is shown by triamidobenzoic acid.

Triamidobenzene combines with two molecules of a monobasic or 1 mol. of a dibasic acid, forming very stable salts. *Triamidobenzene hydrochloride*,  $C^6H^3(NH^2)^3 \cdot 2HCl$ , crystallises in shining needles; it is very soluble in water, but only sparingly in concentrated hydrochloric acid. The *hydriodide* is also readily soluble and forms long radiate needles. *Triamidobenzene sulphate*,  $C^6H^3(NH^2)^3H^2SO^4 + 2H^2O$ , crystallises in large plates (Salkowsky, *Ann. Ch. Pharm.* clxiii. 23).

**Azobenzene**,  $C^6H^5N^2$  or  $C^6H^5-N=N-C^6H^5$ .—*Compound with Benzene*,  $C^6H^5N^2 \cdot C^6H^5$ . This compound separates on cooling from a hot-saturated solution of azobenzene in pure benzene, or better, from a cold-prepared solution by spontaneous evaporation in transparent, thick, oblique rhombic prisms, sometimes an inch long, and differing but little in colour and appearance from azobenzene crystallised from

petroleum. These crystals, when exposed to the air, exhibit an appearance of efflorescence, becoming opaque and of a pale yellowish-red colour, and being converted into easily friable aggregates of small shining crystalline laminae, which retain the external form of the original crystals. This change is due to a loss of benzene. The crystals, heated to 35° in a stream of dry air, give off the whole of their benzene, amounting to 30.6 p. c.; the formula requires 30 p. c. The crystals, heated in a sealed tube, melt at 38° to a dark red liquid, which often retains its fluidity for a long time after cooling to the ordinary temperature.

Azobenzene quickly absorbs benzene vapour. When placed at ordinary temperatures in the state of powder under a bell-jar, together with an open vessel containing benzene, it becomes darker, increases in weight, and is converted into the compound,  $C^{12}H^{10}N^2.C^{12}H^6$ . The absorption of the benzene does not, however, stop at this point; for in a few days the whole of the powder deliquesces to a clear dark red liquid, which still goes on increasing in volume. The exact limit of the absorption has not yet been determined (G. A. Schmidt, *Deut. Chem. Ges. Ber.* v. 1106).

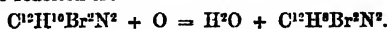
**Bromazobenzenes.**—Werigo (*Ann. Ch. Pharm.* clxv. 189). The brominated compound produced by the action of bromine on azobenzene, and formerly regarded as an addition-product,  $C^{12}H^{10}N^2Br^2$  (1st *Suppl.* 270), appears on further examination to be a substitution-product, viz. dibromazobenzene,  $C^{12}H^8Br^2N^2$ . This conclusion is based on the following facts:—1. The compound is remarkably stable, like azobenzene itself, and unlike the addition-products of the latter, which decompose with facility; the two atoms of bromine are indeed so intimately united with the rest of the group, that they cannot be removed either by the action of silver-salts, or by heating with potash in sealed tubes. 2. Fuming nitric acid converts azobenzene into trinitro-azoxybenzene,  $C^{12}H^7(NO^2)^3N^2O$  (1st *Suppl.* 272), and the brominated body treated with fuming nitric acid, yields—besides the nitro-brominated compounds of azobenzene formerly described—trinitro-dibromo-azoxybenzene,  $C^{12}H^7(NO^2)^3Br^2N^2O$ , as ultimate product. 3. The brominated compound is converted by ammonium sulphide into hydrodibromazobenzene,  $C^{12}H^{10}Br^2N^2$ , just as azobenzene is converted into hydrazobenzene,  $C^{12}H^{12}N^2$ . 4. Digested with warm fuming sulphuric acid, it yields dibromazobenzene-sulphonic acid,  $C^{12}H^8Br^2N^2SO^2.3H^2O$ , analogous to Griess's azobenzenesulphonic acid (1st *Suppl.* 270). 5. The brominated body is produced by treating the alcoholic solution of monobromonitrobenzene with potassium hydrate, just as azobenzene is obtained from nitrobenzene.

Dibromazobenzene dissolves easily in boiling benzene, and separates on cooling in large yellow needles. It is also dissolved readily by carbon sulphide and by chloroform. It melts at 205°, and sublimes without decomposition.

**Tetrabromazobenzene**,  $C^{12}H^6Br^4N^2$ , is obtained as a byo-product in the preparation of dibromazobenzene, and is likewise produced when bromine is added drop by drop to a hot, strong, alcoholic solution of azobenzene. It forms white crystals, very slightly soluble in alcohol, easily soluble in boiling benzene of high boiling point, from which it crystallises on cooling in white silky needles; it is but slightly soluble in chloroform, ether, and carbon sulphide. It melts at about 320°, and then begins to decompose and blacken. Strong nitric acid dissolves it, and the solution mixed with water yields long yellow needles of a substance which explodes when heated.

Werigo once obtained, in the preparation of dibromazobenzene, another product exhibiting the composition of tribromazobenzene,  $C^{12}H^7Br^3N^2$ , but it was not produced on any subsequent occasion.

**Hydrodibromazobenzene**,  $C^{12}H^{10}Br^2N^2$ , is prepared by passing dry ammonia gas and hydrogen sulphide into an alcoholic solution of dibromazobenzene, mixed with an excess of that substance in the solid state; the excess then gradually dissolves, the solution soon becomes colourless, and, on adding water, the hydrodibromazobenzene separates in slender white silky needles, easily soluble in alcohol and ether, and unaffected by exposure to the air. Like hydrazobenzene, it is decomposed in alcoholic solution by nitrous acid, yielding dibromazobenzene, which separates in yellow crystals. The reaction is:



Hydrodibromazobenzene turns red and melts at 130°, and begins to decompose at 160°. When heated to 150° and then cooled, it solidifies to a mass from which hydrochloric acid removes monobromaniline, leaving dibromazobenzene, the decomposition being precisely analogous to that of hydrazobenzene into aniline and azobenzene:—



It has not yet been converted into a compound analogous to bensidine,

Hydrodibromazobenzene appears to be trimorphous. Its concentrated alcoholic solution left to itself in a closed test-tube, deposits, first transparent prismatic crystals, which gradually become opaque on exposure to the air, then yellowish laminae, and lastly, thick yellow crystals. All three forms have the same melting point ( $130^{\circ}$ ), and behave in the same manner when heated.

*Additive Bromine and Chlorine Compounds of Azobenzene.*

(a)  $2C^{12}H^{10}N^2.3HBr$  and  $2C^{12}H^{10}N^2.3HCl$ . The trihydrobromide separates in carmine-red crystals when dry hydrogen bromide is passed into a solution of azobenzene in carbon sulphide or chloroform. When exposed to the air it quickly decomposes into azobenzene and hydrogen bromide, and must be washed with carbon sulphide saturated with hydrogen bromide, in which it is but slightly soluble. It dissolves in pure carbon sulphide and in chloroform, being, at the same time, resolved into azobenzene and hydrogen bromide. Alcohol, ether, and water decompose it in a similar manner. When cautiously heated, it leaves a residue of azobenzene.

The trihydrochloride, prepared like the trihydrobromide, forms yellow crystals still more unstable than the latter.

(b)  $C^{12}H^{10}N^2.HBr.Br^2$ . A body having this composition may be obtained in the three following ways:—(1). By adding excess of phosphorus pentabromide to a solution of azobenzene or azoxybenzene in ether or in chloroform, and heating the mixture. The reaction proceeds quietly, with evolution of hydrogen bromide, and the addition-product (b) separates in crystals which must be washed, not with ether but with carbon sulphide. Both these solvents decompose the compound more or less, but the products formed by carbon sulphide are dissolved at the same time and carried away, leaving the rest of the compound on the filter in its original state. (2). By adding bromine to a solution of the hydrobromide,  $2C^{12}H^{10}N^2.3HBr$ , in chloroform, and washing the crystals which separate with carbon sulphide, containing bromine in solution. (3). By adding bromine and then benzene to a solution of azobenzene in carbon sulphide, and exposing the mixture to sunshine; the bromine-compound then separates in crystals which fill the liquid. The hydrogen bromide required for its formation is generated by the action of the bromine on the benzene: hence the advantage of exposing the mixture to sunshine.

The compound  $C^{12}H^{10}N^2.HBr.Br^2$  is a yellow, crystalline, very unstable body, decomposed by ether, alcohol, carbon sulphide, and chloroform, less, however, by chloroform than by any other of these solvents. From its hot concentrated solution in chloroform it may be partly recovered, in crystals, by rapid cooling. The presence of free bromine in these liquids diminishes their action upon it, and an excess of phosphorus pentabromide is essential in preparing it by the first method in order to diminish the action of the ether. Azobenzene is always reproduced in its decomposition by these liquids, and the whole of the bromine may be precipitated from its alcoholic solution by silver nitrate, silver oxide, or barium peroxide. When cautiously heated or exposed to the air, or left over sulphuric acid under a bell-jar, it decomposes, and finally leaves a residue of azobenzene; but, when prepared by the third method, and generally also when prepared by the first, it likewise yields, on exposure over sulphuric acid an intermediate product, consisting of ruby-red, short, prismatic crystals, which increase in size for a time, and then break up, yielding azobenzene as one of the products of their decomposition; whereas, when prepared by the second method, and occasionally also, when prepared by the first, it passes into azobenzene without the previous formation of these ruby-red crystals. This difference of behaviour might induce the supposition that the processes in question yield two different bodies, perhaps  $C^{12}H^{10}N^2.HBr.Br^2$ , and  $C^{12}H^{10}N^2.2HBr.Br$ ; but, on estimating, by means of sodium thiosulphate, the quantity of free bromine resulting from the decomposition of the compound, this amount is found to be the same in both cases, namely,  $Br^2$ .

(c) The hexbromide,  $C^{12}H^{10}N^2.Br^6$ , separates after some time from a dilute solution of azobenzene in chloroform to which an excess of bromine has been added, in large, dark red, transparent prisms, which decompose very rapidly when removed from the mother-liquor; they may be washed with a solution of bromine in chloroform, and dried in an atmosphere of bromine. The hexbromide is apt to be mixed with a little dibromazobenzene, unless great care has been taken to prevent rise of temperature during its preparation (Werigo, *Ann. Ch. Pharm.* clxv. 203-216).

Azobenzene heated in sealed tubes with fuming hydrochloric acid, is converted, as shown by Ziinin, into benzidine,  $C^{12}H^{12}N^2$ . In this case an addition of  $H^2$  takes place, but the product undergoes an isomeric transformation. The same result is

obtained by boiling azobenzene with fuming hydrobromic acid; also, and with still greater facility, with hydriodic acid.

**Azoxybenzene**,  $C^{12}H^{10}N^2O$ , or  $\begin{array}{c} C^6H^5-N \\ | \\ C^6H^5-N \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} O$ . This compound is not attacked

by strong *hydrobromic acid* at the boiling heat, but when the two substances are heated together in a sealed tube, reaction begins at  $250^\circ$ , and the whole solidifies on cooling to a crystalline mass of dibromaniline hydrobromide. By heating with *hydriodic acid*, azoxybenzene is easily converted into benzidine hydriodide, with separation of iodine. Strong *hydrochloric acid* heated with azoxybenzene in sealed tubes, begins to act upon it at a high temperature, but the tubes then explode (Sendzink, *Zeitschr. f. Chem.* [2] vi. 286).

Azoxybenzene is violently attacked by *phosphorus pentabromide*, with evolution of hydrogen bromide and formation of resinous products; but when the action is moderated by the use of ethereal solutions, yellow crystals are formed, consisting of the compound  $C^{12}H^{11}N^2Br^2$ , or  $C^{12}H^{10}N^2.HBr.Br^2$ , already described (p. 149) (Werigo, *Zeitschr. f. Chem.* [2] vi. 387).

*Phosphorus pentachloride* rapidly converts azoxybenzene into azobenzene, but in ethereal solution a product is formed, apparently similar to that which is obtained with the pentabromide (Werigo, *Ann. Ch. Pharm.* clxv. 203).

*Sodium-amalgam* does not simply reduce azoxybenzene to azobenzene, but converts it into hydrazobenzene, and azoxy-compounds generally into the corresponding hydrazo-compounds (1st Suppl. 270).

**Dibromazoxybenzene**,  $C^{12}H^8Br^2N^2O$ . Sodium-amalgam, which converts nitrobenzene into azobenzene, according to the equation  $2C^{12}H^5NO^2 - O^2 = C^{12}H^{10}N^2$ , does not act in a precisely similar manner on monobromonitrobenzene, so as to produce dibromazobenzene, but takes away only 3 atoms of oxygen instead of 4, producing dibromazoxybenzene:  $2C^{12}H^4BrNO^2 - O^2 = C^{12}H^8Br^2N^2O$ . This substance is yellow, crystalline, easily soluble in hot alcohol and hot benzene, melts at  $175^\circ$  (Werigo, *Ann. Ch. Pharm.* clxv. 198). Hofmann & Goyger (*Deut. Chem. Ges. Ber.* v. 916) by treating an ethereal solution of bromonitrobenzene (melting at  $126^\circ$ ) with sodium, obtained a black substance which, when decomposed by methyl iodide or hydrochloric acid, yielded dibromazoxybenzene, crystallising from alcohol in leaflets, and melting at  $172^\circ$ .

**Trinitro-dibromazoxybenzene**,  $C^{12}H^2Br^2(NO^2)^3N^2O$ , is formed, together with nitrated dibromazobenzenes, by the action of fuming nitric acid on dibromazobenzene. It is crystalline, very slightly soluble in alcohol, melts at  $174^\circ$ , solidifying to a resinous mass on cooling, and decomposes at a higher temperature (*ibid.* 191).

**Dichlorazoxybenzene**,  $C^{12}H^8Cl^2N^2O$ , is formed by heating solid chloronitrobenzene with alcoholic potash. A violent reaction takes place, and the mixture on cooling solidifies to a mass of long, hair-like crystals of dichlorazoxybenzene, melting at  $155^\circ$ – $156^\circ$ , insoluble in water, and slightly soluble in alcohol, from which it is deposited in pale yellow needles having a silky lustre.

The liquid modification of chloronitrobenzene, treated with alcoholic potash, yielded also a small quantity of dichlorazoxybenzene; but this was probably due to the presence of a small quantity of the solid modification, inasmuch as the greater part of the fluid chloronitrobenzene remained unacted upon, even in presence of an excess of potash.

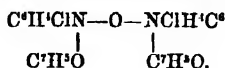
Dichlorazoxybenzene dropped into warm fuming *nitric acid* is dissolved, and the solution, on addition of water, or on cooling, deposits dichloronitrazoxybenzene,  $C^{12}H^7Cl^2(NO^2)^2N^2O$ , as a bright yellow substance, melting at  $134^\circ$ , insoluble in water, and sparingly soluble in alcohol, from which it is deposited in felt-like flocks, consisting of small needles. Its crystals have a beautiful silky lustre, and are difficult to powder. It is apparently reduced by ammonium sulphide, but the product has not been isolated.

Dichlorazoxybenzene added to fuming sulphuric acid, dissolves with slight evolution of heat, the solution at the same time acquiring a metallic reflex, like that of the aniline colours. On cooling, a crystalline substance is deposited, which, when boiled with alcohol and animal charcoal, yields long, reddish-yellow needles of dichlorazobenzene, melting at  $183^\circ$ , insoluble in water, and sparingly soluble in alcohol. Other products appear to be formed at the same time.

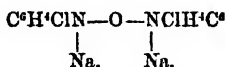
If solid chloronitrobenzene be heated with alcoholic potash, and, after the conversion into dichlorazoxybenzene, the mixture be distilled in a retort, a stage is reached at which a violent reaction takes place, resulting in the formation of chloraniline, which passes over in oily drops, and of dichlorazobenzene, which sublimes in yellowish-red crusts, melting at  $183^\circ$ , and identical with that above described. Dichlorazobenzene treated with ammonium sulphide yields white needles, the nature of which has not yet been determined (K. Heumann, *Deut. Chem. Ges. Ber.* v. 910).

When chloronitrobenzene (melting at  $83^{\circ}$ ) is dissolved in anhydrous ether, and small fragments of sodium are added, the metal is gradually transformed into a black friable substance, which becomes warm and turns yellow on exposure to the air. This substance dissolves in water with red colour, and when heated to  $100^{\circ}$  with ether and methyl iodide, yields a yellow crystalline mass, which, on distillation with water, gives a distillate containing methyl iodide and chloronitrobenzene, melting at  $83^{\circ}$ , and the residue, when crystallised from alcohol, yields dichlorazoxybenzene. The black substance, treated with concentrated hydrochloric acid, yields a yellow crystalline mass similar to that obtained by the action of methyl iodide, and likewise yielding dichlorazoxybenzene.

When the black substance is suspended in ether and treated with benzoyl chloride, an energetic action takes place, the black colour changes to yellow, and the product, distilled with water, gives a distillate containing nitrochlorobenzene. The residue on crystallisation from alcohol yields a substance which has the composition  $C^{10}H^{10}Cl^2N^2O^2$ , crystallises in long prisms, melts at  $125^{\circ}$ , is insoluble in water, and moderately soluble in alcohol or ether. This substance may be regarded as hydro-dichlorazoxybenzene,  $C^6H^4Cl^2N^2O$ , in which two hydrogen-atoms are replaced by benzoyl:—



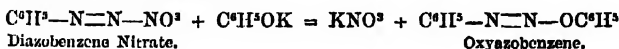
The black substance may be regarded as containing the corresponding sodium compound:—



Dichlorazoxybenzene treated with ammonium sulphide yields, not the corresponding hydro-compound  $C^6H^4Cl^2N^2O$ , as might have been expected, but hydrodichlorazobenzene,  $C^6H^4Cl^2N^2$  or  $C^6H^4Cl-|N-N-NH-C^6H^4Cl$ , a compound formed from dichlorazoxybenzene by substitution of  $H^2$  for  $O$ . This substance crystallises from alcohol in fine colourless crystals, melting at  $122^{\circ}$ . Its alcoholic solution boiled in the air for a long time, or heated to the boiling point with animal charcoal, turns yellow, and deposits crystals of dichlorazobenzene.

Sodium has no action on an ethereal solution of fluid chloronitrobenzene (Hofmann a. Geyger, *Deut. Chem. Ges. Ber.* v. 915).

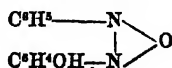
**Oxyazobenzene**,  $C^6H^5N^2O$  or  $C^6H^5-N=N-OC^6H^5$ . This compound, isomeric with azoxybenzene, is formed by the action of potassium phenate in aqueous solution on nitrate of diazobenzene:—



The reaction takes place without evolution of gas, and the oxyazobenzene gradually separates in a brown resinous mass, which soon solidifies in the crystalline form. It agrees in all its properties with the phenol-diazobenzene (azodiphenylamic acid  $C^6H^5O.C^6H^5N^2$ , iv. 433), which Griess obtained, together with phenol-didiazobenzene  $C^6H^5O.2C^6H^5N^2$ , by heating an aqueous solution of diazobenzene nitrate with barium carbonate (Kekulé a. Heideggh, *Zeitschr. f. Chem.* [2] vi. 384). According to Tschervinsky (*Deut. Chem. Ges. Ber.* vi. 560), it crystallises in brick-rod prisms, melting at  $150^{\circ}$  (according to Griess at  $148^{\circ}$ ), dissolves at boiling heat in dilute alcohol and in toluene, slightly in boiling water. Its ammoniacal solution gives with silver nitrate a gelatinous precipitate which becomes crystalline on standing. Nitric acid converts it into picric acid.

**Benzoylazobenzene**,  $C^6H^5(C^6H^5O)N^2O$ , is easily soluble in toluene, sparingly in ether, still less in alcohol, crystallises in tables, nodules, or tetrahedrons, melts at  $136^{\circ}$  (Tschervinsky).

When oxyazobenzene is heated to  $100^{\circ}$  with phosphorus pentachloride, hydrochloric acid is given off; and a body is formed which crystallises from alcohol in long orange-red needles having the composition  $C^{12}H^{10}N^2O^2$ . This body is probably oxy-azoxybenzene,



It is converted by sodium-amalgam into a body which crystallises in yellowish needles: probably the corresponding hydrazo-compound (Kekulé a. Heideggh, *loc. cit.*).

**BENZENE-SULPHONIC ACIDS.**—*Benzene-disulphonic* or *Disulphobenzenic acid*,  $C^6H^4(SO^3H)^2$ . The potassium salt of this acid mixed with potassium cyanide and subjected to dry distillation, yields, together with a large quantity of ammonia, a liquid consisting of benzene, benzonitril, and paradicyanobenzene,  $C^6H^4(CN)^2$  (1 : 4); a liquid which does not boil at  $195^\circ$ , solidifies on cooling, and when boiled with an alkali yields terephthalic acid: hence benzene-disulphonic acid, prepared as above is, for the most part, a para-compound. (Wislicenus a. Brunner, *Deut. Chem. Ges. Ber.* iv. 984).

**Amidobenzene-sulphonic acid**,  $C^6H^4(NH^2).SO^3H$ .—This mixture of isomeric acids, obtained by the action of sulphuric acid on phenol, gives with aniline (amidobenzene), a crystalline product soluble in water and in alcohol. This, when freed from excess of sulphuric acid and cautiously heated, gives off phenol, aniline and sulphurous oxide, and leaves an amidobenzene-sulphonic acid isomeric with Laurent's sulphanic acid, and apparently identical with the sulphanic acid of Gerhardt, Hofmann, Buckton, and Schmitt (v. 477). Pratesi (*Deut. Chem. Ges. Ber.* v. 970).

Amidobenzene-sulphonic acid in aqueous solution is not acted upon by cupric chloride alone; but if, whilst the liquid is boiling, ammonium chloride and a small quantity of ammonia be added, it becomes immediately of a dark red colour. On removing the copper by sulphuretted hydrogen, the colouring matter is reduced, and the liquid becomes brown. On allowing it to remain in contact with air, it is again oxidised, the surface becomes once more red, and on shaking, or on removing the sulphuretted hydrogen by warming, the original colour returns. On evaporation, the colouring matter is obtained. By the addition of a sufficient quantity of copper chloride, amidobenzene-sulphonic acid is completely decomposed. The colouring matter is easily dissolved by water and alcohol, which it colours intensely red; it is completely insoluble in ether and in benzene. It is destroyed by tin chloride and nitric acid; concentrated sulphuric acid dissolves it with brown coloration; on diluting the solution, the characteristic red colour reappears (H. Rose, *Deut. Chem. Ges. Ber.* v. 41).

**Azobenzene-sulphonic acid**,  $C^{12}H^9N^2SO^3$ .—This acid, discovered by Griess (*Ann. Ch. Pharm.* cxxxi. 89; *eliv.* 208), and further examined by Skandarow (*Zeitschr. f. Chem.* [2] vi. 643), is produced by heating azobenzene with fuming sulphuric acid to  $130^\circ$ . The liquid, diluted with a moderate quantity of water, deposits the sulpho-acid, which when re-crystallised from a larger quantity of water, forms shining orange-yellow laminae. Its salts are mostly crystallisable. The potassium salt  $C^{12}H^9KN^2SO^3 + 2H^2O$  crystallises in shining orange-yellow tables; the silver salt  $C^{12}H^9AgN^2SO^3$  also in tables. The barium salt  $Ba(C^{12}H^9N^2SO^3)^2$  is sparingly soluble in water.

The acid fused at a gentle heat with potassium hydrate yields the compound  $C^{12}H^9N^2O$ , identical with phenol-diazobenzene or azodiphenylamic acid (iv. 433); and by treating this compound with ammonium sulphide, a base is produced, probably  $C^{12}H^{12}N^2O$ .

By saturating an ammoniacal solution of azobenzene-sulphonic acid with hydrogen sulphide, evaporating and precipitating with hydrochloric acid, benzidine-sulphonic or hydrazobenzene-sulphonic acid,  $C^{12}H^{12}N^2SO^3$ , is obtained. This acid dissolves sparingly in hot water and crystallises therefrom in yellow needles or laminae. Its barium salt  $Ba(C^{12}H^{12}N^2SO^3)^2$  crystallises in light yellow shining laminae. The acid does not dissolve in ammonia or other alkalis, but is resolved thereby into benzidine and sulphuric acid.

**Azobenzene-sulphonic Chloride**,  $C^{12}H^9N^2SO^3Cl$ , is formed by treating potassium azobenzene-sulphonate dried at  $165^\circ$  with phosphorus pentachloride. The action commences at ordinary temperatures, but must be completed by heating for a few hours in the water-bath, after which the product may be mixed with water, and the precipitated solid chloride dried and crystallised from pure ether. It forms loosely-coherent orange-yellow nodules, insoluble in water, and slowly resolved by boiling with water into hydrochloric and azobenzene-sulphonic acid. It dissolves in alcohol, and is decomposed thereby, without however yielding an ether. It is also decomposed by ammonia and by boiling potash (Skandarow).

**Azobenzene-sulphamide**,  $C^{12}H^9N^2SO^3NH^2$ , is prepared by treating the chloride with strong ammonia. The reaction begins spontaneously, and is attended with rise of temperature. The product is heated in the water-bath to expel the excess of ammonia; the sal-ammoniac formed in the reaction is dissolved out by cold water; and the amide, after drying, is re-crystallised from boiling alcohol. It is an orange-yellow powder, insoluble in water, slightly soluble in boiling alcohol, insoluble in caustic alkali; gives off ammonia when boiled with potash (Skandarow).



**Dibromobenzene-sulphonic acid**,  $C^6H^2Br^2N^2SO^3 + 3H^2O$ . When a warm solution of dibromobenzene in fuming sulphuric acid is digested for some time, and then poured into boiling water, the liquid becomes filled with yellow crystals of the brominated sulpho-acid, provided a certain quantity is present; if more or less than this particular quantity of water has been taken, the acid remains in solution. It thus resembles azobenzene-sulphonic acid in being soluble both in water and in strong sulphuric acid, as well as in the mode of its production. It is monobasic, and dissolves easily in water, alcohol, and ether, the solutions having an acid reaction. A hot concentrated aqueous solution gelatinises when suddenly cooled, but gradually becomes filled with crystals. It occurs in three forms, appearing under the microscope as very slightly coloured needles, broad yellow plates, and reddish crystals pointed at both ends.

The *potassium salt* resembles the free acid in appearance, but is less soluble in water and still less in alcohol. From its hot alcoholic solution it separates on cooling in orange-yellow needles. The *silver salt* is a yellow, amorphous powder, very slightly soluble in water and in alcohol (Werigo).

**Oxyazobenzene-sulphonic acid**,  $C^{12}H^8N^2O.SO^3H$ , obtained by heating oxyazobenzene in the water-bath with 3 or 4 parts of fuming sulphuric acid, and purified by separation from its barium salt, crystallises in well-defined octohedral combinations, and is easily soluble in water. The sparingly soluble *barium salt*  $Ba(C^{12}H^8N^2O.SO^3)^2 + 2H^2O$  crystallises in gold-yellow laminae. The easily soluble *copper salt* and the *magnesium salt* contain  $6H^2O$ ; the *potassium salt* is anhydrous (Tschirvinsky, *Deut. Chem. Ges. Ber.* vi. 560).

**Bromobenzene-sulphonic acid**,  $C^6H^4Br.SO^3H$ .—According to A. Ross-Garrick, the acid formed by the action of bromine on benzene-sulphonic acid is isomeric, not identical, with that which Couper obtained by dissolving bromobenzene in sulphuric acid, differing from the latter, partly by the forms of its salts, but more especially in apparently yielding hydroquinone when fused with potash, whereas Couper's acid yields resorcin. According to Genz, on the other hand, the isobromobenzene-sulphonic acid prepared by the action of bromine on benzene-sulphonic acid yields resorcin as well as hydroquinone by fusion with potash (*1st Suppl.* 274).

To throw further light on this question, the behaviour of isobromobenzene-sulphonic acid with potassium hydrate has been re-examined by A. Wölz (*Zeitschr. f. Chem.* [2] vii. 449; *Ann. Ch. Pharm.* clxviii. 88), who obtained an oily product, exactly as described by Garrick, only partially soluble in water; the aqueous solution left on spontaneous evaporation a dark-coloured crystalline residue, from which, by sublimation, pure resorcin was obtained. Pure hydroquinone was ascertained to give no trace of its isomerides when similarly sublimed, nor was it altered by fusion with potassium hydrate, so that the resorcin cannot have been a product of the conversion of hydroquinone.

Further, potassium isobromobenzene-sulphonate was distilled with potassium cyanide, whereby a liquid and a solid product were obtained: the former gave benzoic, the latter terephthalic acid on treatment with alkali. The results obtained with potassium hydrate and with potassium cyanide are, therefore, in complete accordance, and necessitate a re-examination of the two series of salts.

**Bromobenzene-sulphochloride**,  $C^6H^4BrSO^2Cl$ , is produced by dissolving bromobenzene with gentle heat in fuming sulphuric acid, neutralising the solution with lime, separating the calcium salt of the bromobenzene-sulphonic acid from the gypsum by extraction with boiling water, converting it into the corresponding sodium salt, and heating the latter in the dry state with the calculated quantity of phosphorus pentachloride in a capacious flask till the entire mass becomes liquid. After cooling, the sulphochloride is washed with water and dissolved in ether free from alcohol, from which it crystallises with great facility, forming large shining prismatic crystals belonging to the triclinic system, and exhibiting the combination  $P \infty . \frac{P}{2} . OP$ . It

melts at  $75-76^\circ$  (Hübner u. Alsborg, *Zeitschr. f. Chem.* [2] vi. 389).

**Bromobenzene-sulphydrate**,  $C^6H^4BrSH$ , is formed by heating the sulphochloride with tin and concentrated hydrochloric acid, the liquid then turning blue. It volatilises with vapour of water, dissolves easily in hot, slowly in cold alcohol, and crystallises in white laminae resembling naphthalene, and melting at  $75^\circ$ . The alcoholic solution forms with *lead acetate* a bright yellow precipitate; with *mercuric chloride* a heavy white precipitate, both insoluble in water and in alcohol; with *cupric acetate* and *silver nitrate* it forms dirty yellow precipitates (Hübner u. Alsborg).

**Dibromobenzene-sulphonic acid**,  $C^6H^2Br^2.SO^3H$ , is obtained by dissolving dibromobenzene in Nordhausen sulphuric acid, diluting with water, neutralising with

lime, decomposing the resulting calcium salt with sulphuric acid, and dissolving out the sulpho-acid with alcohol; or, better, by neutralising with lead carbonate and decomposing the lead salt with hydrogen sulphide.

The sulpho-acid crystallises in silky needles, which gradually change into compact plates. It contains 2 mol. water of crystallisation, and melts at about  $117^{\circ}$ , becoming brown at the same time.

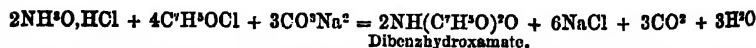
Its *calcium salt*  $(C^6H^3Br^2SO^3)^2Ca + 4H^2O$  forms long colourless needles, very soluble in water; the *silver salt*  $C^6H^3Br^2SO^3Ag + 3H^2O$  transparent needles, also very soluble. The *lead salt*  $(C^6H^3Br^2SO^3)^2Pb + 3H^2O$  crystallises from a saturated solution in fine, long, six-sided prisms, which change after some time into largo, compact, rhombic tables. The *barium salt*  $(C^6H^3Br^2SO^3)^2Ba + 2H^2O$ , the *sodium salt*  $C^6H^3Br^2SO^3Na + 1\frac{1}{2}H^2O$ , and the *potassium salt*  $C^6H^3Br^2SO^3K + H^2O$ , are very soluble in water; the first crystallises in four-sided tables, the other two in needles (R. Douglas Williams, *Zeitschr. f. Chem.* [2] vii. 302. Hübner a. Williams, *Ann. Ch. Pharm.* clxvii. 117).

This acid has also been prepared in the same manner as above by A. Wölz (*ibid.* 353; further, *Ann. Ch. Pharm.* clxviii. 81), whose results agree for the most part with those of Williams. He finds, however, that the crystallised acid contains 3 mol. water of crystallisation, only 2 of which are given off at  $100^{\circ}$ , the remainder at about  $120^{\circ}$ , at which temperature the acid undergoes further decomposition. According to Wölz, also, the *calcium salt* contains 9 mol. water instead of 4, as found by Williams; the *barium salt* dried over sulphuric acid is anhydrous; the *copper salt*  $(C^6H^3Br^2SO^3)^2Cu$  forms long shining laminae, apparently containing  $14H^2O$ ; the *ammonium salt*  $C^6H^3Br^2SO^3(NH^4)$  crystallises, from a concentrated solution, in shining needles, and by slow evaporation in compact plates. Wölz believes that his dibromobenzeno-sulphonic acid is identical with that of Williams, and isomeric with that which Schmitt obtained some years ago by decomposing dibromodiazobenzene-sulphonic acid with boiling alcohol (*Ann. Ch. Pharm.* cxx. 158).

*Dibromonitrobenzene-sulphonic acid*,  $C^6H^2Br^2(NO^2).SO^3H$ , is obtained as a viscous mass on boiling dibromonitrobenzene with fuming nitric acid. The *potassium salt*  $C^6H^2Br^2NO^2SO^3K + 2\frac{1}{2}H^2O$  forms small needles, soluble in alcohol and water; the *barium salt*  $(C^6H^2Br^2NO^2SO^3)^2Ba + 2\frac{1}{2}H^2O$  groups of small needles. The *copper salt*  $(C^6H^2Br^2NO^2SO^3)^2Cu + H^2O$  is very soluble in water, alcohol, and ether; on evaporating the latter solution, it remains as a syrup, in which crystalline nodules gradually appear. The *lead salt*  $(C^6H^2Br^2NO^2SO^3)^2Pb + H^2O$  forms very small, reddish needles, sparingly soluble in water. The *strontium salt* is very soluble, and crystallises in microscopic needles (Hübner a. Williams, *Ann. Ch. Pharm.* clxvii. 121).

**BENZHYDROXAMIC ACIDS.** (Lossen, *Ann. Ch. Pharm.* clxii. 347).—The successive replacement of the 3 atoms of hydrogen in hydroxylamine  $NH^3O$  by benzoyl, gives rise to two acids, namely, benzhydroxamic,  $NH^2(C^6H^5O)O$ , and dibenzhydroxamic,  $NH(C^6H^5O^2)O$ , while the replacement of the third atom in like manner produces a neutral body  $N(C^6H^5O^2)O$ , called tribenzhydroxylamine.

*Preparation of Benzhydroxamic and Dibenzhydroxamic Acid.*—Benzoyl chloride poured into an aqueous solution of hydroxylamine or its hydrochloride supersaturated with soda, is almost entirely converted into benz- and dibenz-hydroxamic acid. The two acids being produced simultaneously,



1 part of hydroxylamine salt is dissolved in 8 to 10 parts of water with sufficient soda to take up all the chlorine set free by the reaction, and 3 parts benzoyl chloride are added gradually with constant agitation, keeping the mixture cold. The sparingly soluble dibenzhydroxamic acid which separates should be recrystallised from alcohol, and the benzhydroxamic acid, which remains for the most part in solution, may be obtained by precipitating with baryta-water, decomposing with sulphuric acid, purifying the product by crystallisation from a small quantity of warm alcohol, and washing the crystals with ether. The hydroxylamine solution for this preparation may be obtained by digesting tin for a week in the cold with nitric acid, hydrochloric acid and water, and precipitating the tin with soda (1st Suppl. 723).

**Benzhydroxamic Acid**,  $NH^2(C^6H^5O)O$ .—The pure acid crystallises in colourless rhombic plates, exhibiting the forms  $\infty P$ ,  $\infty \bar{P}$ ,  $\bar{P}$ ,  $\bar{P}$ , and cleaving perfectly

parallel to  $\infty P \infty$ . Ratio of axes  $a : b : c = 0.325563 : 1 : 0.321707$ . The crystals are strongly double-refractive, and have the plane of the optic axes parallel to  $bc$  (Klein, *Ann. Ch. Pharm.* clxvi. 180). The acid dissolves in 44.5 parts of water at  $6^\circ$ , much more easily in warm water, very easily in alcohol, sparingly in ether and in carbon sulphide, and not at all in benzene. The impure acid forms warty masses. It has an acid reaction, and melts at  $124.5^\circ$ . The acid and its salts are decomposed more or less violently at a high temperature. Heated with dilute hydrochloric or sulphuric acid, it splits up into benzoic acid and a salt of hydroxylamine.

Benzhydroxamic acid is monobasic, but has a tendency to form acid salts. The acid potassium salt  $\text{NH}(\text{C}^2\text{H}^3\text{O})\text{OK} \cdot \text{NH}^2(\text{C}^2\text{H}^3\text{O})\text{O}$ , and the acid sodium salt  $\text{NH}(\text{C}^2\text{H}^3\text{O})\text{ONa} \cdot \text{NH}^2(\text{C}^2\text{H}^3\text{O})\text{O} + 3\text{H}^2\text{O}$ , form rhombic prisms or plates, moderately soluble in warm water, little soluble in alcohol. The sodium salt effloresces in dry air. An alcoholic solution of the free acid treated with potash gives a precipitate of the acid salt, redissolved by further addition, but reappearing in crystals as the solution evaporates in air.

The neutral barium salt is obtained in microscopic needles when the acid potassium salt, neutralised with ammonia, is treated with barium chloride. If the ammonia be omitted, a variable mixture of neutral and acid barium salt is precipitated. The latter crystallises in small prisms, together with the free acid, when the neutral salt is decomposed with an insufficient quantity of sulphuric acid, and the filtrate allowed to evaporate. It is nearly insoluble in water and alcohol. The calcium and zinc salts are neutral: the former is an amorphous, the latter a crystalline precipitate.

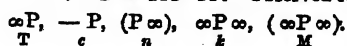
Solutions of the acid sodium salt give white precipitates with manganous chloride, cadmium sulphate, alum and lead nitrate, nearly white with cupric sulphate, green with chrome alum, whitish green with nickel sulphate, peach-coloured with cobalt nitrate, yellow with mercuric chloride, all soluble in excess; white with silver nitrate, rapidly blackening, and insoluble in excess. Ferric chloride gives a dark red precipitate, soluble with intense red colour in excess, or in dilute sulphuric or hydrochloric acid. The latter when concentrated destroys the colour, but it appears again on dilution.

**Dibenzhydroxamic Acid**,  $\text{NH}(\text{C}^2\text{H}^3\text{O})^2\text{O}$ , crystallises by cooling in needles or prisms, by spontaneous evaporation of the alcoholic solution in shining rhombic crystals, which, according to Klein, exhibit the faces  $0P$ ,  $\infty P \infty$ ,  $\infty P$ ,  $2P \infty$ ,  $P \infty$ ,  $2P \infty$ , and cleave perfectly parallel to  $\infty P$ ; they exert strong double refraction, and have the plane of the optic axes parallel to  $bc$ . The acid dissolves with difficulty in water, cold alcohol, ether, or carbon sulphide, more easily in hot alcohol, not at all in benzene. It has an acid reaction, melts at  $145^\circ$ , decomposes violently at a higher temperature, with formation, among other products, of benzanilide. With acids it splits up like benzhydroxamic acid; with alkalis it gives a benzoate and a benzhydroxamate. The latter, by slaking with benzoyl chloride and water, may be reconverted into dibenzhydroxamic acid.

The acid is monobasic and forms neutral salts. The potassium salt  $\text{N}(\text{C}^2\text{H}^3\text{O})^2\text{OK}$  crystallises from alcohol in pearly, very thin plates, or microscopic six-sided tables, decomposing with violence by heat, and leaving a benzoate and a sparingly soluble indifferent body. The aqueous solution decomposes on standing, without, however, producing benzhydroxamic acid. The sodium salt is rather more soluble in alcohol than the potassium salt, and forms sharp-pointed prisms.

A fresh solution of potassium dibenzhydroxamate gives white precipitates with manganous chloride, with lead, silver, and cobalt nitrates, and with zinc and cadmium sulphates; blue-green with chrome alum; apple-green with nickel sulphate; and with ferric chloride a reddish-yellow precipitate but no coloration. It is distinguished from benzhydroxamate and oxalhydroxamate by giving no precipitate with salts of the alkaline earths.

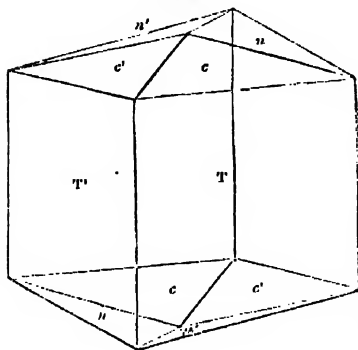
**Tribenzhydroxylamine**,  $\text{N}(\text{C}^2\text{H}^3\text{O})^3\text{O}$ , is among the products of the action of a solution of benzoyl chloride in a hydrocarbon boiling at  $110^\circ$ , on dry hydroxylamine hydrochloride. It is also formed by heating potassium dibenzhydroxamate to  $100^\circ$  with benzoyl chloride in excess, afterwards removing the benzoyl chloride with ether and the potassium chloride with water, and recrystallising the residue from alcohol. It is insoluble in water, ether, and benzene, nearly insoluble in cold, but easily soluble in boiling alcohol, from which it crystallises in groups of small shining prisms. These crystals (fig. 5), are monoclinic, having the axes  $a : b : c = 1.15835 : 1 : 0.334900$ , and the angle of the inclined axes  $bc = 83^\circ 21' 20''$ . Angle  $-P : -P = 149^\circ 24'$ ;  $\infty P : \infty P = 96^\circ 36'$ ;  $-P : \infty P = 118^\circ 14'$ . Observed forms:—



The plane of the optic axes coincides with the clinodiagonal principal section, and the two principal directions of vibration are so situated in this plane that one runs nearly

parallel to  $P\infty$ , the other nearly at right angles to it (Klein, *loc. cit.*). Tribenzhydroxylamine melts at  $140^\circ$ , and decomposes at  $190^\circ$ . Its alcoholic solution treated with potash splits up into benzoate and dibenzhydroxamate.

FIG. 5.



Tribenzhydroxylamine admits probably of only one rational formula; but benzhydroxamic and dibenzhydroxamic acid admit each of two: the first may be either  $\text{NH}(\text{C}^6\text{H}_5\text{O})(\text{HO})$  or  $\text{NH}^+(\text{OC}^6\text{H}_5\text{O})$ , the second  $\text{N}(\text{C}^6\text{H}_5\text{O})(\text{HO})$  or  $\text{NH}(\text{C}^6\text{H}_5\text{O})(\text{OC}^6\text{H}_5\text{O})$ .

#### BENZHYDRYL-BENZOIC ACID.

See BENZOYL-BENZOIC ACID.

#### BENZIDINE, $\text{C}^{12}\text{H}^{12}\text{N}^2 = \text{C}^{12}\text{H}^6(\text{NH}^2)^2$ .

—The cyanide of this base,  $\text{C}^{12}\text{H}^{12}\text{N}^4.2\text{CN}$ , is formed when benzidine, prepared from azobenzene, decolorised by boiling with animal charcoal, and purified by several recrystallisations from alcohol, is dissolved in alcohol, and cyanogen gas is passed into the solution till the liquid smells strongly of it. The liquid, if then left to itself for two days, deposits benzidine cyanide as a red mass, the quantity of which gradually increases. This compound appears amorphous under the microscope; it is insoluble in water, slightly soluble in alcohol, ether, and benzene, somewhat more freely in light petroleum oil, but even in this liquid it is not sufficiently soluble to admit of purification by solution and separation. It is resolved by acids into benzidine and oxalic acid (Wittenstein, *Deut. Chem. Ges. Ber.* iii. 723).

**Nitrobenzidines.**—Benzidine treated with nitric acid yields only oxidation-products, no nitro-compounds. To obtain the latter, benzidine must first be converted into acetobenzidine, which is easily effected by boiling benzidine with glacial acetic acid for two hours.

**Acetobenzidine**,  $\text{C}^{12}\text{H}^6(\text{NH}.\text{C}^6\text{H}_5\text{O})^2$ , is insoluble in water, and crystallises from hot alcohol in white needles. It is a very stable compound, not so easily decomposed by stronger acids as acetanilide.

Cold nitric acid converts it into **dinitracetobenzidine**,  $\text{C}^{12}\text{H}^6(\text{NO}^2)(\text{NH}.\text{C}^6\text{H}_5\text{O})^2$ , a yellow crystalline powder which, when boiled with caustic potash, yields **dinitrobenzidine**,  $\text{C}^{12}\text{H}^6(\text{NO}^2)(\text{NH}^2)^2$ , a light red crystalline powder, insoluble in water, but soluble in hot alcohol, from which solution it separates after some time in larger crystals having a beetle-green lustre. The **hydrochloride** forms shining dark yellow plates, and is a very unstable body, being readily decomposed by water as well as by heat.

Dinitrobenzidine does not appear to be convertible into amidobenzidine by the action of reducing agents. By acting on the dinitro-compound with tin and hydrochloric acid, the nitrogen of the nitro-group is separated in the form of ammonia, and benzidine is formed, whilst by heating it with ammonium sulphide only indefinite brown substances are obtained.

On digesting benzidine with carbon sulphide, the compound  $\text{C}^{12}\text{H}^6\left\{\begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}\right\}\text{CS}$  is obtained, a body quite insoluble in all common solvents. Besides this substance, another, having the same composition, but soluble in alcohol, is formed in smaller quantity, to which perhaps the above formula should be given, whilst the insoluble body might be a polymeride (Strakosch, *Deut. Chem. Ges. Ber.* v. 236).

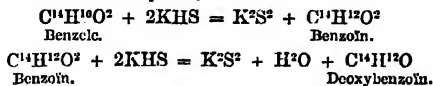
**Benzidine-disulphonic acid** or **Hydrazobenzene-sulphonic acid**,  $\text{C}^{12}\text{H}^{12}\text{N}^2\text{SO}_3$ , is formed by the action of ammonium sulphide on azobenzene-sulphonic acid (see page 152).

**Base homologous with Benzidine**,  $\text{C}^{14}\text{H}^{10}\text{N}^2$  (Petrie, *Zeitschr. f. Chem.* [2] vi. 265). This base is obtained as a hydrochloride or sulphate when strong hydrochloric or sulphuric acid is added by drops to an alcoholic solution of hydrazotoluene prepared from azotoluene by the action of sodium-analgam; hydrazotoluene prepared with ammonium sulphide does not yield it. The aqueous solution of the hydrochloride treated with ammonia deposits the base in colourless transparent laminae having a silvery lustre. These crystals are easily soluble in boiling water, soluble also in alcohol and in ether, melt at  $128^\circ$ – $129^\circ$ , and decompose at a higher temperature.

The **hydrochloride**,  $\text{C}^{14}\text{H}^{10}\text{N}^2.2\text{HCl}$ , crystallises in colourless laminae, which dissolve

easily in water, but separate from the solution on addition of strong hydrochloric acid. It is insoluble in alcohol and ether. The aqueous solution forms a yellow crystalline precipitate with platinic chloride. There are two *sulphates*, which resemble one another in external characters, but differ in solubility, the one being soluble, the other insoluble in hot water and in alcohol. The insoluble salt, which has the composition  $C^{11}H^{10}N_2 \cdot 2HCl$ , is a white pulverulent mass, partially decomposed by water, the liquid gradually turning reddish.

**BENZILE**,  $C^{11}H^{10}O^2$ .—This compound distilled with soda-lime yields, together with benzene, considerable quantities of benzophenone or diphenyl ketone,  $C^{14}H^{10}O^2 = CO + CO(C^6H^5)^2$ . Heated with potassium sulphhydrate, to  $120^\circ$ , it is converted into benzoin and toluylene oxide or deoxybenzoin:



(Jena, *Ann. Ch. Pharm.* clv. 77).

**Benzile tetrachloride**,  $C^{11}H^{10}O^2Cl^4$ , treated with zinc in alcoholic solution yields two isomeric compounds,  $C^{11}H^{10}Cl^4$ , the first of which forms white rhombic plates, melting at  $153^\circ$ , and dissolving in 10 parts of boiling alcohol, whereas the second crystallises in long needles or six-sided prisms, which melt at  $63^\circ$  and dissolve in any quantity of boiling alcohol; 10 parts of the tetrachloride yield 2.2 to 2.4 parts of the first and 6 to 5.2 parts of the second compound. Both these compounds dissolve without decomposition in ether and acetic acid. They are not attacked by zinc, or by alcoholic potash at  $130^\circ$ ; sodium-amalgam, on the other hand, converts them into toluene (Zinin, *Zeitschr. f. Chem.* [2] vii. 284).

**Dinitrobenzile**,  $C^{11}H^8(NO^2)^2O^2$ .—Benzile treated with boiling fuming nitric acid, yields two isomeric *dinitrobenziles*, one crystallising in octohedrons which melt at  $131^\circ$  and dissolve in 41 parts of boiling and 137 parts of cold alcohol; the second crystallising in plates, which melt at  $147^\circ$  and dissolve in 52.5 parts of boiling and 230 parts of cold alcohol (Sagmenny, *Deut. Chem. Ges. Ber.* v. 1100).

**BENZILIC ACID**,  $C^{11}H^{12}O^3$  (Jena, *Ann. Ch. Pharm.* clv. 77).—This acid is formed by heating benzile with water, or better with alcoholic potash:



Benzile dissolves in alcoholic potash with deep violet colour, and its conversion into benzoic acid takes place sometimes at ordinary temperatures, the liquid becoming heated to the boiling point of the alcohol, sometimes only after heating over a gas flame. After the reaction is ended, the liquid must be heated till it becomes light yellow, then mixed with water and precipitated with hydrochloric acid. If the benzoic acid is only slightly contaminated with benzoic acid, it may be completely purified by one or two crystallisations from hot water. If a larger quantity of benzoic acid is present, it is best to digest the precipitate with a quantity of sodium carbonate not sufficient to dissolve it completely; the benzoic acid is then chiefly dissolved, and may be precipitated from the filtrate by hydrochloric acid and recrystallised from hot water.

Benzilic acid was originally obtained by oxidation of benzoin,  $C^{11}H^{12}O^2$  (i. 515), and is commonly said to be formed from that substance also by the action of alcoholic potash; according to Jena, however, this takes place only when the benzoin is contaminated with benzile; and according to Limpricht & Schwanert (*Deut. Chem. Ges. Ber.* iv. 336), the products obtained by heating benzoin with alcoholic potash are different, according as the reaction takes place in an open flask or in sealed tubes. In the former case the benzoin is partly converted by the oxidising action of the air, into benzile—the formation of which is rendered evident by the deep violet colour which the liquid assumes from the beginning of the action,—and the benzile is then converted into benzoic acid as above. When, on the other hand, the reaction takes place in sealed tubes, no benzoic acid is obtained, or only a trace—and the liquid exhibits the violet coloration above mentioned only at the commencement of the reaction, a small quantity of benzile being then formed by the oxidising action of the air in the tube.

Benzilic acid crystallises in small monoclinic needles, which have a white colour and satiny lustre, but assume a fine reddish colour at  $110^\circ$ , melt at  $150^\circ$ ,\* the liquid

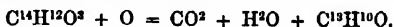
\* It is commonly stated that benzoic acid melts at  $120^\circ$ ; this, however, is the melting point of benzoic acid, which is often formed in considerable quantity simultaneously with benzoic acid, by the action of alcoholic potash on benzile, and when contaminated with traces of benzoic acid, exhibits the red coloration characteristic of the latter when heated or acted upon by sulphuric acid.

becoming deep red at a higher temperature; the same colour is produced by treatment with strong sulphuric acid, but disappears on addition of water. It has a bitter taste; dissolves easily in alcohol, ether and hot water, very sparingly in cold water.

**Barium Benzilate**,  $\text{Ba}(\text{C}^{11}\text{H}^{11}\text{O}^3)^2 + 6\text{H}^2\text{O}$ , obtained by dissolving the acid in baryta-water, decolorising with animal charcoal and evaporating, forms white crusts. The silver salt obtained by precipitation is white, but becomes dark coloured, gradually at ordinary temperatures, more quickly when heated. *Ethyl benzilate* is precipitated on adding water to the alcoholic solution of benzilic acid mixed with hydrochloric acid, as a yellow oil, which has an odour of peppermint, does not crystallise, and is decomposed by distillation.

Benzilic acid heated for several hours to  $180^\circ$  is converted into a deep red liquid, which solidifies on cooling to an amorphous mass easily soluble in alcohol. On evaporating the alcoholic solution thus obtained, several compounds crystallise out, among which are dibenzilic acid  $\text{C}^{28}\text{H}^{20}\text{O}^3 = 2\text{C}^{14}\text{H}^{10}\text{O}^3 - \text{H}^2\text{O}$ , and benzophenone  $\text{C}^{18}\text{H}^{10}\text{O}$ . A similar decomposition appears to take place when benzilic acid is heated to  $150^\circ$  with hydrochloric acid. By dry distillation benzilic acid yields a red-brown empyreumatic oil, which may be distilled with aqueous vapour, but carbonises when heated alone to  $270$ – $280^\circ$ . Benzilic acid is not altered by heating to  $150^\circ$  for three hours with alcoholic potash.

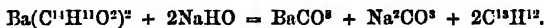
By oxidising substances, chromic acid for example, benzilic acid is converted into carbon dioxide, water, and benzophenone:



Benzophenone is likewise formed by the dry distillation of silver benzilate, or by prolonged boiling of that salt with water.

Barium benzilate distilled with  $\frac{1}{10}$ th of its weight of *soda-lime* is resolved into carbon dioxide and benzhydrol:  $\text{C}^{14}\text{H}^{12}\text{O}^3 = \text{CO}^2 + \text{C}^{14}\text{H}^{12}\text{O}$ .

**Deoxybenzyllic Acid**,  $\text{C}^{14}\text{H}^{12}\text{O}^2$ .—Benzilic acid is not acted upon by sodium-amalgam or by zinc and hydrochloric acid; but when heated to  $150^\circ$  with concentrated *hydriodic acid*, it is reduced to deoxybenzyllic acid. On digesting the product with water, dissolving the residue in aqueous sodium carbonate, and acidulating with hydrochloric acid, the deoxybenzyllic acid is precipitated, and may be purified by crystallisation from hot water or from alcohol, separating from the former in needles resembling those of benzilic acid, from the latter in large laminæ. It is sparingly soluble in cold water, but dissolves easily in hot water, also in alcohol and ether; melts at  $146^\circ$ , and when more strongly heated yields a small sublimate, but does not turn red, like benzilic acid. Heated with strong sulphuric acid, it assumes a greenish-yellow colour. By oxidation with chromic acid it yields the same products as benzilic acid. Its silver salt  $\text{AgC}^{14}\text{H}^{11}\text{O}^2 + 2\text{H}^2\text{O}$  obtained by precipitation from a neutralised solution, forms small needles blackening on exposure to light. The barium-salt  $\text{Ba}(\text{C}^{14}\text{H}^{11}\text{O}^2)^2 + 2\text{H}^2\text{O}$  is easily soluble in water, and crystallises in tufts of satiny needles, melting above  $300^\circ$ . This salt distilled with a small quantity of soda-lime yields diphenyl-methane,  $\text{C}^{18}\text{H}^{12}$  or  $\text{CH}_2\left\{\begin{smallmatrix} \text{C}^6\text{H}^5 \\ \text{C}^6\text{H}^5 \end{smallmatrix}\right.$ :



The diphenyl-methane passes over as an oil, crystallises at low temperatures, and when purified by solution in alcohol, decoloration with animal charcoal, evaporation, and recrystallisation in a freezing mixture, forms monoclinic prisms, having a very fragrant odour, like that of oranges, melting at  $26.4^\circ$ , soluble in ether and in alcohol. The ethereal solution gives a precipitate after a while with bromine (Jena).

Benzilic acid is regarded by Städeler and by Lämpricht a. Schwanert, as *diphenylglycollic acid*  $\text{C}(\text{OH})(\text{C}^6\text{H}^5)^2\text{CO}^2\text{H}$ , and deoxybenzyllic acid as *diphenyl-acetic acid*  $\text{CH}(\text{C}^6\text{H}^5)^2\text{CO}^2\text{H}$  (see Benzoin).

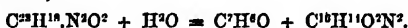
**Ethyl-benzilic acid**,  $\text{C}^{18}\text{H}^{16}\text{O}^3 = \text{C}^{14}\text{H}^{11}(\text{C}^6\text{H}^5)\text{O}^3$ .—A body having this composition is formed, together with several other products, when benzoïn is heated with sodium-alcohol to  $160^\circ$  in sealed tubes (4 grams of benzoïn with 1 gram of sodium dissolved in 20 c. c. spirit of 92 p. c., for two or three hours). On evaporating off the alcohol, mixing the slightly yellowish residue with water, filtering after 12 hours, and treating the filtrate with hydrochloric acid, ethyl-benzilic acid is precipitated, together with a little benzoic acid and a very small quantity of benzilic acid. These two acids may be removed by cold solution of sodium carbonate, which leaves the ethyl-benzilic acid undissolved; and, on washing with water, dissolving the residue in alcohol or ether, and evaporating, ethyl-benzilic acid remains as a light-yellow uncrystallisable mass, having the consistence of turpentine.

Ethyl-benzilic acid distils apparently unaltered, leaving only a small residue. Heated with strong sulphuric acid, it turns first red-brown, then dark brown, but not red like benzilic acid. It is insoluble in water, but dissolves easily in alcohol and ether, the alcoholic solution having an acid reaction. It does not dissolve in cold solution of sodium carbonate or in ammonia, and is nearly insoluble in aqueous potash, but dissolves very easily on addition of a little alcohol. Boiled with baryta-water, it partly dissolves, and is reprecipitated by hydrochloric acid, while another portion is converted into a viscid adhesive resin probably a barium-compound. The alcoholic solution of ethyl-benzilic acid gives a precipitate with neutral lead acetate and a little ammonia, none with silver nitrate, even on careful addition of ammonia. The alcoholic solution, mixed with a small quantity of soda-ley, forms with silver nitrate a white precipitate, which, after drying, turns brown even at a gentle heat. Ethyl-benzilic acid is not altered by heating to  $160^{\circ}$  for three hours with alcoholic potash, or by digestion in alcoholic solution with sodium-amalgam. Heated to  $170^{\circ}$  with hydriodic acid, it yields a brown mass insoluble in alcohol and in sodium carbonate. Bromine acts but feebly on it even with the aid of heat, forming resinous products.

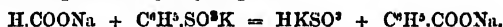
It will be seen from the preceding description, that the acid properties of this compound are by no means well defined; indeed, it is doubtful whether the name ethyl-benzilic acid can be appropriately applied to it. (Jena a. Limpricht, *Ann. Ch. Pharm.* clv. 100).

Respecting the constitution of benzilic acid and its derivatives, see Benzoin.

**BENZIMIDE.** Laurent's benzimide,  $C^{12}H^{11}N^2O^2$ , produced by the action of hydrocyanic acid on bitter almond-oil, is resolved by heating with water to  $160$ – $180^{\circ}$  into benzoic aldehyde and the imide of formo-benzilic (mandelic) acid (Zinin, *Deut. Chem. Ges. Ber.* iii. 552):



**BENZOIC ACID,**  $C^7H^5O^2$ .—This acid is formed by fusing a dry mixture of sodium formate and potassium phenylsulphite:



By dissolving the fused mass in water, distilling after acidulation, neutralising the distillate with sodium carbonate, boiling it with animal charcoal to remove sulphur-compounds, then concentrating by evaporation, and acidulating with hydrochloric acid, benzoic acid is separated, and may be obtained perfectly pure by recrystallisation from water and sublimation (V. Meyer, *Deut. Chem. Ges. Ber.* iii. 112).

Löwe (*J. pr. Chem.* cviii. 257) finds that when gum benzoin is dissolved in alcohol of 95 p. c. and the filtered solution is mixed with alcoholic soda, it deposits after 48 hours a red-brown substance, the aqueous solution of which gives with hydrochloric acid an amorphous precipitate, which, when heated, yields an abundant sublimate of benzoic acid. Hence Löwe infers that the greater part of the benzoic acid does not exist in the resin ready formed—since, in that case, it would have gone down in the soda-precipitate and would have been precipitated in the crystalline form on addition of hydrochloric acid to the aqueous solution of that precipitate—but is produced by the action of heat on a substance previously existing in the resin. The acid filtrate did indeed yield on evaporation a small quantity of benzoic acid, which probably existed in the resin in the free state. The formation of benzoic acid from the resin by heat does not depend on the action of the air, for Löwe found that the same quantity of the acid product is obtained by heating the gum benzoin with an equal weight of sulphuric acid (free from nitric acid), to  $170^{\circ}$ . The mixture, contained in a leaden dish, is placed in a shallow vessel of iron or copper covered with the usual paper cover, and having fixed to its side a vertical glass tube within which a thermometer is placed. The heat must be applied slowly, as otherwise the mass is apt to froth over.

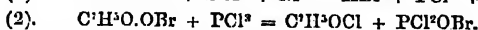
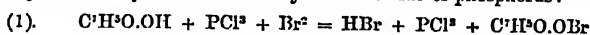
According to Guichard (*Null. Soc. Chim.* [2] xix. 359), benzoic acid may be advantageously extracted from gum benzoin by means of carbon sulphide. Having left a quantity of benzoin macerating for some time with carbon sulphide, he found it covered with colourless crystals of benzoic acid, and the liquid on evaporation yielded a further crop of nearly pure crystals.

The following determinations of the melting points of mixtures of benzoic and cinnamic acids are given by J. Kachler (*Zeitschr. f. Chem.* [2] vi. 60):—

Benzoic Acid	Cinnamic Acid	Melting Point	Benzoic Acid	Cinnamic Acid	Melting Point
100 p.c.	0	123.3°	40	60	98.7°
99	1	118.2	30	70	108.2
90	10	111.5	20	80	118.0
80	20	106.4	10	90	126.6
70	30	101.4	1	99	131.8
60	40	87.1	0	100	133.3
50	50	84.3			

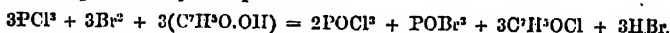
Hence it appears that the lowest melting point is exhibited by a mixture of the two acids in equal proportions.

**Reactions.**—1. When *bromine* is added by drops to a mixture of 1 mol. benzoic acid and 1 mol. *phosphorus trichloride*, a violent action takes place, hydrobromic acid being given off, and the mass gradually becoming liquid. The product when subsequently distilled, yields benzoyl chloride and oxychlorobromide of phosphorus:



Phosphorus pentachloride acts in a similar manner (Wichelhaus, *Deut. Chem. Ges. Ber.* i. 77).

According to Gauthier et. Michaelis (*Jenaische Zeitschrift*, vi. 242), the action of bromine and phosphorus trichloride on benzoic acid takes place in a different manner, namely, as represented by the equation:



When 40 grams of benzoic acid, 45.2  $\text{PCl}^3$ , and 52.4 bromine were made to act on one another as described by Wichelhaus, and the mass afterwards fractionated, it separated into a portion boiling at 110°–115° and another passing over at 150°–190°, whereas nothing was obtained having a boiling point of 135°–137° (oxychlorobromide of phosphorus.) From the higher-boiling portion, by cooling and addition of a crystal of phosphorus oxybromide, a portion was obtained in the crystalline state, having the properties and composition of the oxybromide. The greater part of the latter, however, remained dissolved in the benzoyl chloride,

2. When benzoic acid is fused with *potassium hydrate* at 360° for about half-an-hour, paraoxybenzoic acid is formed, together with a yellow amorphous body,  $\text{C}^{10}\text{H}^7\text{O}^2$ , and brown resinous bodies. A small quantity of a crystalline acid,  $\text{C}^{14}\text{H}^{12}\text{O}^2$ , easily soluble in alcohol and ether, and giving a violet-red colour with ferric chloride, is likewise produced by the further action of the fused potash on the paraoxybenzoic acid.

3. When benzoic acid is fused with an equal weight of *potassium sulphocyanate*, the reaction commences at 150°, and is terminated at 170°. Carbon oxysulphide, sulphuretted hydrogen, and carbon sulphide are evolved, and a residue is left, consisting principally of benzamide, which can easily be purified by crystallisation. The yield is large, amounting to 81 p.c. of the benzoic acid taken, so that this method can be advantageously employed for the preparation of benzamide.

When potassium sulphocyanate is distilled with two molecules of benzoic acid, scarcely anything but benzonitril is formed (as previously shown by Letts), so that it would seem that the potassium benzoate formed during the reaction abstracts water from the benzamide, forming benzonitril. Benzamide distilled with potassium benzoate yields benzonitril. Ammonium benzoate, on the contrary, has no action on benzamide (Kekulé, *Deut. Chem. Ges. Ber.* vi. 110).

**Metallic Benzoates.**—Several of these salts have been examined by Sestini, Ciognani et. Zavatti (*Bull. Soc. Chim.* [2] xiii. 488). The *potassium salt*  $\text{K}^2\text{C}^6\text{H}^5\text{O}^2 + 3\text{H}^2\text{O}$  is obtained by spontaneous evaporation of its solution, in irregular whitish laminae, which effloresce and fall to powder on exposure to the air. By evaporation under a bell jar over sulphuric acid, colourless anhydrous needles are obtained.

*Sodium Benzoate*,  $\text{NaC}^6\text{H}^5\text{O}^2 + \text{H}^2\text{O}$ , forms small efflorescent nodules made up of microscopic prisms.

The *magnesium salt*  $\text{Mg}(\text{C}^6\text{H}^5\text{O}^2)^2 + \text{H}^2\text{O}$  is obtained by spontaneous evaporation over sulphuric acid, in spherical masses composed of small oblique prisms, or by evaporating the solution till a crystalline film forms on the surface, as a white laminated mass.



The *zinc salt*,  $\text{Zn}(\text{C}^7\text{H}^5\text{O}^2)^2$  crystallises in oblique prisms when its concentrated solution is left to cool, and in shining laminae united in arborescent masses when left to evaporate over sulphuric acid. It is more soluble in cold than in hot water: consequently a solution saturated in the cold becomes turbid when heated, and deposits part of the salt in the anhydrous state.

The *nickel salt*  $\text{Ni}(\text{C}^7\text{H}^5\text{O}^2)^2 + 3\text{H}_2\text{O}$  crystallises by spontaneous evaporation in light green crusts. It is efflorescent, slightly soluble in cold, more soluble in hot water.

The *cobalt salt*  $\text{Co}(\text{C}^7\text{H}^5\text{O}^2)^2 + 2\text{H}_2\text{O}$  forms delicate, shining, longitudinally striated laminae, which are colourless when viewed separately, but appear peach-blossom-coloured in mass. When heated it gives off its water and acquires a fine blue-violet colour.

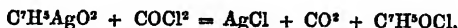
The *copper salt*  $\text{Cu}(\text{C}^7\text{H}^5\text{O}^2)^2 + 2\text{H}_2\text{O}$  is a light blue precipitate, slightly soluble in cold, abundantly in hot water, and crystallising therefrom in thin, light blue, rhomboidal laminae united in spherical groups; when heated it gives off its water and becomes deep blue.

*Tin salts.* Benzoates yield insoluble precipitates both with stannous and with stannic chloride. The stannous precipitate is reddish and appears to have the composition  $\text{Sn}(\text{C}^7\text{H}^5\text{O}^2)^2 + \text{H}_2\text{O}$ . The white precipitate obtained with stannic chloride appears to be a molecular compound of stannic hydrate with benzoic acid,  $\text{SnH}^4\text{O}^4 \cdot \text{C}^7\text{H}^5\text{O}^2 + 9\text{H}_2\text{O}$ .

The *aluminium salt*,  $\text{Al}^3 \left\{ \begin{array}{l} (\text{C}^7\text{H}^5\text{O}^2)^2 \\ (\text{OH})^2 \end{array} \right\} + \text{H}_2\text{O}$ , forms white, easily soluble crystals, grouped in dendritic forms.

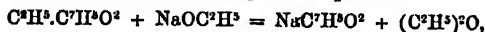
The ferrous and ferric salts were not obtained in the crystalline form.

*Silver benzoate*, treated with bromine, yields benzoic acid and a resinous body (Dunze, *Zeitschr. f. Chem.* [2] vii. 119). With *liquid phosgene* it forms benzoyl chloride:

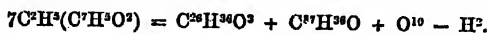


A small quantity of a chlorinated oil, probably  $\text{C}^7\text{H}^5\text{Cl}^2$ , is formed at the same time (V. Meyer, *Zeitschr. f. Chem.* [2] vi. 496).

*Ethyl Benzoate*,  $\text{C}^2\text{H}^5\text{C}^7\text{H}^5\text{O}^2$ .—This ether, treated with sodium ethylate, yields sodium benzoate and ethyl oxide, according to the equation:



besides formic acid, and two oily bodies, one of which has the composition  $\text{C}^{10}\text{H}^{10}\text{O}^3$  (or perhaps  $\text{C}^{10}\text{H}^{10}\text{O}^2$ ), and the other  $\text{C}^{10}\text{H}^{10}\text{O}$ . Their formation may perhaps be represented by the equation:



The production of formic acid may be due to the action of the liberated oxygen on the benzoic ether (Geuther, *Jenaische Zeitschrift*, vii. 126).

**Bromobenzoic acids.**—Parabromobenzoic or bromodracrylic acid, obtained by oxidising bromotoluene with chromic acid, melts at  $251^\circ$ ; metabromobenzoic acid, produced by the action of bromine on benzoic acid, melts at  $153^\circ$  (*1st Suppl.* pp. 309, 310). The ortho-modification, or bromo-salicylic acid, does not appear, to have been obtained. V. v. Richter indeed states that it is formed, together with the meta-acid, by the action of bromine on benzoic acid; but this statement is contradicted by Hübner a. Petermann (*Ann. Ch. Pharm.* cxlix. 131), who found that only one brominated acid (the meta-acid) is formed in this way; also by Hübner a. Friedburg (*ibid.* elviii. 19), who obtained in this same manner a mixture of metabromobenzoic with unaltered benzoic acid. Such mixtures often melt at temperatures lower than the melting points of either of their constituents; thus a mixture of 2 parts benzoic with 1 part bromobenzoic acid melts at about  $190^\circ$ , and a mixture of 1 part benzoic with 5 parts bromobenzoic acid at about  $115^\circ$ . This circumstance has probably given rise to the supposition that two brominated acids are formed by the action of bromine on benzoic acid. Peligot, by treating silver benzoate with bromine, obtained a brominated acid melting at  $100^\circ$  (i. 534), and Angerstein (*Ann. Ch. Pharm.* elviii. 1) has shown that the product thus obtained is a mixture of bromobenzoic with benzoic acid; further that the bromobenzoic acid separated from it, agrees with metabenzoic acid in its melting point ( $153^\circ$ ), in the characters of its barium salt, which crystallises in small smooth needles, and in those of its nitro-acid.

Metabromobenzoic acid then is formed by the action of bromine on benzoic acid, on silver benzoate, and on benzamide (*1st Suppl.* 315), whence it appears that the three groups  $\text{COOH}$ ,  $\text{COOAg}$ ,  $\text{CONH}^2$ , have the same influence on the bromine-atom, causing it to stand to the group  $\text{COOH}$ , &c. in the position 1 : 3. Moreover, it is known that the

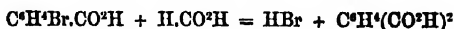
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presence of the group  $\text{CH}^3$  gives rise to the formation of a para-compound, bromo-toluene  $\text{C}^6\text{H}_4\text{CH}^3$  being converted by oxidation into para-oxybenzoic acid; hence it appeared possible that the presence of the group  $\text{CN}$  might cause the formation of orthobromobenzoic acid. On heating benzonitrile,  $\text{C}^6\text{H}_5\text{CN}$ , with bromine in closed tubes, a reddish-brown thick liquid was obtained, which was dissolved in alcohol, and the solution diluted with water; microscopic crystals gradually separated out, which were scarcely attacked by caustic potash solution at  $120^\circ$ . From the alkaline liquid a small quantity of an acid was obtained, melting at  $230^\circ$ – $235^\circ$ , which was probably parabromobenzoic acid. Other experiments to prepare the missing or orthobromobenzoic acid, likewise gave only negative results. As Henry has shown, this acid is not formed, as chlorosalicylic acid (orthochlorobenzoic acid) is, by treating salicylic acid with phosphorus pentabromide, and decomposing the product with water. Friedburg found, like Henry, that only bromosalicylic acid is thereby formed. He tried further to prepare diazo-orthoamidobenzoic acid, in order to convert it by the action of hydrobromic acid into metabromobenzoic acid, but did not succeed in obtaining the diazo-compound, which appears to be a most unstable body. On mixing a solution of the sulphate of ortho-amidobenzoic acid (anthranilic acid) with potassium nitrate in the cold, and adding hydrobromic acid, nitrogen is evolved, but no orthobromobenzoic acid is formed; the solution containing only salicylic and nitro-salicylic acids, which shows that the diazo-compound is decomposed by the water before the hydrobromic acid can act upon it (Friedburg, *Ann. Ch. Pharm.* clviii. 29).

Friedburg further confirms the results of Hübner, Ohly, and Philipp, that by treating pure meta-bromobenzoic acid with strong nitric acid, two isomeric bromonitrobenzoic acids are formed, viz. *α*-bromonitrobenzoic acid, which melts at  $250^\circ$ , and the *β*-acid melting at  $140^\circ$  (1st Suppl. 315, 316).

Potassium bromobenzoate fused with sodium formate yields isophthalic acid, together with benzoic acid. The formation of isophthalic acid is represented by the equation:



(Ador a. Meyer, *Deut. Chem. Ges. Ber.* iv. 359).

*Dibromobenzoic acid*,  $\text{C}^6\text{H}^2\text{Br}^2\text{O}^2$  (Hübner n. Angerstein, *loc. cit.*). This acid is best obtained by enclosing 5 grams of benzoic acid and 13.1 grams of bromine in tubes, half filled with water and heating them to  $200^\circ$ – $230^\circ$ , until the colour has nearly disappeared. The resulting mixture of mono-, di-, and tri-bromobenzoic acid is boiled with water and barium carbonate, and the solution concentrated. Tribromobenzoate then crystallises out first, and afterwards impure dibromobenzoate; whilst the salt of the mono-bromobenzoic acid remains in the mother-liquor. The complete separation of the three acids is very difficult, and can only be effected by employing large quantities of material.

*Barium dibromobenzoate*,  $\text{Ba}(\text{C}^6\text{H}^2\text{Br}^2\text{COO})_2 + 2\text{H}_2\text{O}$ , crystallises in fine, short, transparent needles. The calcium salt forms shining plates; the sodium salt is very soluble, and does not crystallise well; the silver salt forms a white, and the copper salt a light green precipitate. Pure dibromobenzoic acid is sparingly soluble in water, readily in ether and alcohol, and crystallises in tufts of slender needles, melting at  $223^\circ$ – $227^\circ$ , and subliming without decomposition.

Silver monobromobenzoate treated with bromine does not yield dibromobenzoic acid, the product consisting of silver bromide, monobromobenzoic acid, and a few drops of a volatile oil, which attacks the eyes powerfully.

*Dibromonitro-benzoic acid*,  $\text{C}^6\text{H}^2\text{Br}^2\text{NO}^2\text{COOH}$ . To prepare the compound, impure dibromobenzoic acid is dissolved in hot concentrated nitric acid. The solution is evaporated on the water-bath, and the residue dissolved in sodium carbonate. As the sodium salt of the acid crystallises exceedingly well, it is easily obtained by recrystallising the mixture of the sodium salts, rejecting the first crystals and the last mother-liquors. The middle portion yields, on further crystallisation, the pure salt  $\text{NaC}^6\text{H}^2\text{Br}^2(\text{NO}^2)\text{COO}^2 + 3\text{H}_2\text{O}$ , which separates from a hot concentrated solution in large shining leaflets, and from a diluted solution in long fine needles. When heated it deflagrates, leaving a bulky, carbonaceous mass behind.

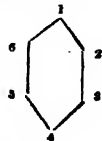
*Barium dibromonitrobenzoate*,  $\text{Ba}(\text{C}^6\text{H}^2\text{Br}^2\text{NO}^2\text{COO})_2 + 2\text{H}_2\text{O}$ , forms fine silky needles. The strontium salt crystallises in very long and fine silky needles. The lead and silver salts are white precipitates, and the copper salt forms a light green precipitate. The acid crystallises from water in white needles, which melt at  $182^\circ$ , and deflagrate on further heating.

*Dibromamido-benzoic acid*,  $\text{C}^6\text{H}^2\text{Br}^2(\text{NH}^2)\text{COOH}$ , is obtained by boiling dibromonitro-benzoic acid for a short time with tin and strong hydrochloric acid. On adding water to the cold solution, the amido-acid, which does not combine with hydrochloric acid, is

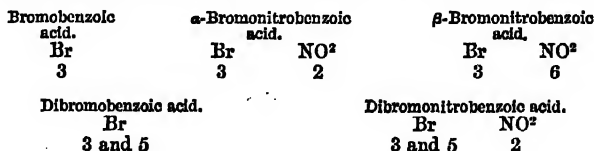
precipitated; it crystallises from boiling water in microscopic needles, and from dilute alcohol in distinct needles: it melts at 196°, and decomposes on stronger heating. By sodium-amalgam it is converted into *ortho*-amido-benzoic (anthranilic) acid. The mother-liquor from the preparation of this compound contains *metamido-benzoic acid*.

The relative positions of the radicles in the above-described brominated derivatives

of benzoic acid may be represented as follow, regarding bromo-benzoic



acid as a meta-compound, and supposing that the carboxyl is combined with carbon No. 1 of the benzene nucleus:—



**Bromochlorobenzoic acids** (Claus a. Pfeiffer, *Deut. Chem. Ges. Ber.* v. 656).—The three chlorobenzoic acids are not all converted with equal ease into the corresponding bromochlorobenzoic acids by the action of bromine on their aqueous, alcoholic, or ethereal solutions. Chlorosalylic acid is scarcely altered even after heating with bromine in sealed tubes, whereas chlorobenzoic acid is acted upon with comparative readiness. They may all be easily brominated, however, by the action of bromine on a hot solution of the silver salt.

**Bromochlorosalylic acid** crystallises in fine, small, glistening needles, melting at 151°, and soluble in 380 parts of water at 21°. Like chlorosalylic acid, it melts under boiling water, but is more soluble than that acid. Its salts are also more soluble than the corresponding chlorosalylates.

**Bromochlorobenzoic acid** also crystallises in fine, white, felted needles, but is less soluble than the above (1080 parts of water at 21° dissolve 1 part of the acid), and does not melt under boiling water. Its barium salt crystallises with two molecules of water; that of the above-mentioned isomeric acid contains three.

In the preparation of chlorobenzoic acid by the action of potassium chlorate and hydrochloric acid on benzoic acid, somewhat considerable quantities of dichlorobenzoic acid are formed. The properties of the acid thus obtained differ in several respects from those described as characteristic of dichlorobenzoic acid by Otto, and by Beilstein and Kuhlberg.

The two acids above described appear to be converted into dioxy-benzoic acids by fusion with potassium hydrate. This appears to succeed if the temperature be carefully regulated, but if the heating be carried too far, chlorobromosalylic acid yields considerable quantities of salicylic acid.

**Chlorobenzoic acids.**—Parachlorobenzoic or chlorodraeylic acid heated in a sealed tube to 200° with antimony pentachloride is converted into dichlorobenzoic acid boiling at 201°, and identical in every respect with that which is obtained by the action of chloride of lime on benzoic acid, &c. &c. (*1st Suppl.* 312).

In this acid, therefore, the two chlorine-atoms occupy the para- and meta- positions, that is to say, its formula is  $C^HClHHCLO^2H$ . *Ortho*-chlorobenzoic (chlorosalylic) acid similarly treated would probably yield an isomeric dichlorobenzoic acid (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] vi. 417).

Another modification of dichlorobenzoic acid is obtained, together with the mono-chlorinated acid, by the action of potassium chlorate and hydrochloric acid on benzoic acid in diffused daylight. It crystallises in soft, silky, interlaced needles, melting at 158°, and subliming without decomposition. Its barium salt  $Ba(C^H^2Cl^2O^2)^2 + 3H^2O$  forms long, thin lustrous needles, which dissolve in 12.5 parts water at 28°. The calcium salt  $Ca(C^H^2Cl^2O^2)^2 + 2H^2O$  crystallises in slender radiated needles (Claus, *Deut. Chem. Ges. Ber.* 721).

Otto, by boiling dichlorhippuric acid with strong hydrochloric acid, obtained a dichlorobenzoic acid, melting at 196°–197°; its calcium and barium salts have, however,

the same form and composition as those of the acid obtained by Claus (*Ann. Ch. Pharm.* cxxii. 129; cxxiii. 216).

**Trichlorobenzoic acid**,  $C^6H^3Cl^3.CO^2H$ . A trichlorobenzoic acid, isomeric with that produced from trichlorotoluene-trichloride (1st *Suppl.* 312), is obtained by heating chrysanic (amido-dinitrobenzoic) acid with concentrated hydrochloric acid for nine hours to  $200^{\circ}$ – $210^{\circ}$ . On opening the tubes, torrents of nitrogen and carbon dioxide escape, and the residue contains ammonium chloride and some nitro-products. This reaction, which may be represented by the equation:

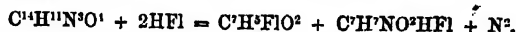


affords the first example of the replacement of amido- and nitro-groups by chlorine.

The trichlorobenzoic acid thus obtained, crystallises from dilute alcohol in fine needles, melting at  $203^{\circ}$ , but subliming at a lower temperature; it is almost insoluble in cold, and sparingly soluble in boiling water. Its *silver salt*  $AgC^6H^3Cl^3O^2$  is a white precipitate crystallising from boiling water in microscopic needles. The *barium salt*  $Ba(C^6H^3Cl^3O^2)^2 + 4H^2O$  crystallises from a hot solution in small prisms. The *calcium salt*  $Ca(C^6H^3Cl^3O^2)^2 + 6H^2O$  is but slightly soluble in cold water, and crystallises from a hot solution in small shining needles. The *ethyl ether* is insoluble in water, and crystallises from alcohol in slender needles melting at  $86^{\circ}$ .

The *chloride*,  $C^6H^3Cl^3.CO^2Cl$ , obtained by the action of phosphorus pentachloride on the acid, is readily soluble in ether, benzene, and carbon sulphide, and forms hard prisms, melting at  $36^{\circ}$ , and having a faint but pungent odour. The *amide*,  $C^6H^3Cl^3.CONH^2$ , produced by heating the chloride with ammonia, is readily soluble in alcohol and ether, and crystallises in small needles melting at  $176^{\circ}$  (Salkowski, *Ann. Ch. Pharm.* clxiii. 33).

**Fluobenzoic acid**,  $C^6H^5FO^2$  (Schmitt a. Gehren, *J. pr. Chem* [2] i. 394). Hydrofluoric acid decomposes diazo-amidobenzoic acid in a manner similar to hydriodic and hydrochloric acids, producing fluobenzoic and hydrofluoro-amidobenzoic acids, with evolution of nitrogen:



The mixture of the two acids was gently heated in a platinum dish till it had become entirely fluid, and the evolution of nitrogen had ceased. On cooling, the crude fluobenzoic acid crystallised out, and was purified, first by treatment with animal charcoal and crystallisation from water, and finally by solution in ether, in order to separate the hydrofluoro-amidobenzoic acid which remained undissolved. Fluobenzoic acid crystallises in colourless rhombic prisms very similar to benzoic acid. It volatilises readily at  $100^{\circ}$ , melts at  $182^{\circ}$ , and solidifies at  $170^{\circ}$ . It dissolves with difficulty in cold water, but easily in hot water, alcohol and ether. It has a strong acid reaction, expels carbonic acid from the alkaline carbonates, and does not etch glass. It is soluble without decomposition in concentrated sulphuric acid and with nitric acid it forms nitrofluoro-benzoic acid.

With the metals, fluobenzoic acid forms neutral salts which crystallise well from their aqueous solutions. The *silver salt*, prepared by precipitating the ammonium salt with silver nitrate, and recrystallising, forms yellow plates having the composition  $AgC^6H^5FIO^2$ . The *calcium salt*  $Ca(C^6H^5FIO^2)^2 + 3H^2O$ , obtained by neutralising the acid with calcium carbonate, crystallises in large prisms. The *barium salt*  $Ba(C^6H^5FIO^2)^2 + 4H^2O$  was prepared in a manner similar to the calcium salt. *Ethyl fluobenzoate* was obtained by saturating an alcoholic solution of the acid with dry hydrochloric acid; it crystallises, and may be volatilised without decomposition. Calcium fluobenzoate distilled with 4.3 times its weight of calcium hydrate is decomposed, with formation of fluobenzene  $C^6H^5F$  (p. 142).

**Iodobenzoic acid**.—The iodobenzoic acid which Griess obtained by the action of hydriodic acid on sulphate of diazosallylic acid (from anthranilic acid) crystallises in long white needles, which may be readily sublimed. It dissolves somewhat in hot, very sparingly in cold water, very easily in cold ether and alcohol; melts at  $132^{\circ}$ . This is doubtless the ortho-acid. Another modification which Griess obtained by the action of hydriodic acid on diazobenzo-amidobenzoic acid melts at  $185^{\circ}$ , and this is most probably the meta-acid, inasmuch as Körner has obtained the para-acid (iododraeylic acid) and found it to melt at  $260^{\circ}$  (Griess, *Deut. Chem. Ges. Ber.* iv. 188; *Chem. Soc. J.* [2] ix. 702). See also 1st *Suppl.* p. 313.

**Nitrobenzoic acids**.—Ortho-nitrobenzoic acid (not hitherto known) is produced by oxidising ortho-nitrocinnamic acid with chromic acid. That the nitrobenzoic acid thus obtained is really the ortho-acid is proved by its conversion into

ortho-amidobenzoic or anthranilic acid by reduction with tin and hydrochloric acid, and conversion of the latter into salicylic acid by the action of nitrous acid.

Crude nitro-cinnamic acid (which likewise contains the para-acid), may be used for the preparation, inasmuch as the para-nitrobenzoic acid formed at the same time is much less soluble than the ortho-acid, and therefore easily separated from it.

Orthonitrobenzoic acid crystallises from water in small needles readily soluble in cold alcohol and ether. It melts at  $141^{\circ}$ , the same temperature at which metanitrobenzoic acid melts, but differs from the latter by being more soluble in water (100 parts of water dissolving at  $16.5^{\circ}$ , 0.61 parts of the ortho-acid and only 0.235 of the meta-acid); the barium and zinc salts of the former are also more soluble than the salts of the meta-acid. The barium salt  $\text{Ba}[\text{C}_6\text{H}_4(\text{NO}_2)\text{O}]^2 + 3\text{H}_2\text{O}$  forms radiated crystalline groups. The calcium salt  $\text{Ca}[\text{C}_6\text{H}_4(\text{NO}_2)\text{O}]^2 + 2\text{H}_2\text{O}$  is very soluble in water, and crystallises in small thin needles. The lead salt  $\text{Pb}[\text{C}_6\text{H}_4(\text{NO}_2)\text{O}]^2 + \text{H}_2\text{O}$  crystallises in small shining prisms, sparingly soluble in cold water. The zinc salt is obtained in a syrup which gradually crystallises. The ethylic ether melts at  $30^{\circ}$ . The amide  $\text{C}_6\text{H}_4(\text{NO}_2).\text{CONH}^2$  crystallises in short needles (Beilstein a. Kuhlberg, *Ann. Ch. Pharm.* clxiii. 134).

*Dinitrobenzoic acid*,  $\text{C}_6\text{H}_3(\text{NO}_2)^2.\text{CO}^2\text{H}$  (Tiemann a. Judson, *Deut. Chem. Ges. Ber.* iii. 223. Murctow, *Zeitschr. f. Chem.* [2] vi. 641).—1. From *Dinitrotoluene*. When pure dinitrotoluene is heated for some time with fuming nitric acid, especially at  $100^{\circ}$  under pressure, the unaltered dinitrotoluene then removed by precipitation with water, and the filtrate evaporated, crystals of dinitrobenzoic acid are obtained, which may be purified from small quantities of adhering dinitrotoluene by solution in aqueous sodium carbonate. The acid precipitated from the solution by dilute nitric acid may be recrystallised from boiling water, in which it first melts, then dissolves and separates in long prisms on cooling. In the dry state it melts at  $179^{\circ}$ . It sublimes without decomposition and forms well crystallised salts. The lead, barium, and silver salts are soluble in water, and may be recrystallised therefrom (Tiemann a. Judson).

2. From *Mononitrobenzoic acid*.—When pure nitrobenzoic acid melting at  $127^{\circ}$  is continuously heated with a mixture of fuming nitric and fuming sulphuric acid, and the cooled mixture is diluted with water, dinitrobenzoic acid separates after a while in shining crystals, an additional quantity of which may be obtained by partially neutralising the excess of nitric and sulphuric acids present with sodium carbonate, or by shaking the acid liquid with ether (Tiemann a. Judson). Murctow boils 100 grams of nitrobenzoic acid with 300 grams of fuming nitric acid, sp. gr. 1.48—1.49, and 600 grams of oil of vitriol, as long as red fumes are given off (four or five hours), and then leaves it to cool, whereupon the pure dinitro-acid crystallises out; this may be drained on asbestos, and the rest of the dissolved acid precipitated by water, in which, in fact, it is less soluble than in weak nitric acid. To purify it from adhering mono-nitrobenzoic acid, it may be combined with ammonia, precipitated with silver nitrate, and crystallised from water; the less soluble silver dinitrobenzoate then crystallises out first, in needles; or the acid may be combined with baryta, whereupon needles of the mononitrated salt separate first; if they are mixed with nodules, the quantity of water added has not been sufficient. The solution is to be precipitated with hydrochloric acid, and the precipitate recrystallised from water; 35 grams of nitrobenzoic acid yield by this process 15 grams of the dinitro-acid.

Cahours, who discovered dinitrobenzoic acid, prepared it by heating benzoic acid with a mixture of nitric and sulphuric acids (*1st Suppl.* 557). According to Murctow, this process yields only the mono-nitrated acid. As, however, this acid is converted by the same treatment into the dinitro-acid, it is difficult to understand how some quantity of the latter can fail to be produced when benzoic acid is subjected to the prolonged action of a mixture of sulphuric and nitric acids.

Dinitrobenzoic acid prepared as just described is nearly insoluble in cold, somewhat soluble in boiling water (1 part in 53 according to Murctow) and crystallises therefrom on cooling in shining laminae, which melt when dry at  $202^{\circ}$ , but begin to sublime at a lower temperature (Tiemann a. Judson). According to Murctow, it crystallises from water in square plates, which gradually become larger, but remain so thin that they exhibit the finest interference colours. It dissolves in alcohol more freely than in water, and separates in large, transparent, well-defined prisms, melting at  $204^{\circ}$ — $205^{\circ}$ .

Dinitrobenzoic acid forms dark red solutions with alkalis and with baryta-water. It dissolves in a small quantity of strong aqueous ammonia, and the solution deposits crystals which dissolve in a larger quantity of ammonia, like those of the mononitrated acid. With excess of ammonia, a red solution is formed which becomes colourless on boiling, and then deposits crystals of ammonium dinitrobenzoate. The barium salt

$\text{Ba}\{\text{C}^6\text{H}^4(\text{NO}^2)_2\text{O}^2\}^2 + 5\text{H}_2\text{O}$  crystallises from water in pale yellow nodules; acetates when heated. The silver salt is yellowish when recently precipitated, but crystallises from water in nearly colourless needles. It is permanent in the air and detonates when heated (Muretow).

The differences of melting point and crystalline form of the dinitrobenzoic acids prepared from dinitrotoluene and from mononitrobenzoic acid, show that they are isomeric, not identical.

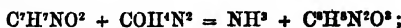
Dinitrobenzoic acid heated in alkaline solution with sodium-amalgam, is converted into a black humus-like body, having the composition of diazoxybenzoic acid,  $\text{C}^6\text{H}^3\text{N}^2\text{O}^3$  (Meyer a. Michler, p. 168).

Trinitrobenzoic acid,  $\text{C}^6\text{H}^2(\text{NO}^2)_3\text{CO}^2\text{H}$ , is obtained by digesting trinitrotoluene with fuming nitric acid at  $100^\circ$  in sealed tubes; the transformation, however, is not complete, even when the action is continued for a fortnight. The unaltered trinitrotoluene having been precipitated by water and the liquid filtered, the filtrate on evaporation deposits trinitrobenzoic acid in large well-defined prismatic crystals which may be further purified in the manner above described for the dinitro-acid. Pure trinitrobenzoic acid melts at  $190^\circ$  when dry, and sublimes without decomposition. Its ammonium salt is crystallisable. The silver salt crystallises in reddish laminae, slightly soluble in water. When the free acid is heated with an excess of alkali, especially of ammonia, it first turns red and then decomposes (Tiemann a. Judson).

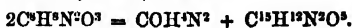
#### Reduction-derivatives of the Nitrobenzoic Acids.

**Amidobenzoic acids**,  $\text{C}^6\text{H}^4(\text{NH}^2)\text{O}^2 = \text{C}^6\text{H}^4(\text{NH}^2)\text{COOH}$ .—*Meta-amido-benzoic acid*. When this acid is treated with carbon bisulphide in alcoholic solution, hydrogen sulphide is evolved and dicarboxyl-sulphocarbonyl  $\text{N}^2 \left\{ \begin{array}{l} \text{OS}^2 \\ \text{C}^6\text{H}^3 \\ \text{H}^2 \end{array} \right.$   $\text{COOH}^2$ , is separated in white needles (Merz a. Weith, *Zeitschr. f. Chem.* [2] vii. 46).

*Carboxamidobenzoic and Uramidobenzoic acids* (Griess, *J. pr. Chem.* [2]. iv. 292; v. 369).—When amidobenzoic acid and urea are melted together at a moderate heat, uramidobenzoic or oxybenzuramic acid,  $\text{C}^6\text{H}^3\text{N}^2\text{O}^3$  (*ibid.* Suppl. 318) is formed:



and this acid, if kept at the temperature of  $20^\circ$ , is gradually resolved into urea and carboxamidobenzoic acid,  $\text{C}^6\text{H}^4\text{N}^2\text{O}^3$ :



This method of preparation consequently yields a mixture of the two acids, the relative quantities depending on the time and temperature.

By heating amidobenzoic ether with urea, the ethers of both the above acids are obtained; and from this mixture uramidobenzoic ether may readily be extracted by hot water. It melts at  $176^\circ$ ; carbamidobenzoic ether at  $162^\circ$ .

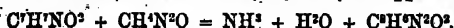
Uramidobenzoic ether is easily prepared by adding hydrochloric solution of amidobenzoic ether to aqueous solution of potassium cyanate. This ether is identical with the one obtained by the method given above; and the carboxamidobenzoic ether obtained from it by the action of heat, is identical with that mentioned above. These two ethers may also be obtained by the action of cyanic acid upon alcoholic solution of amidobenzoic acid. A compound is thus formed having the composition  $\text{C}^6\text{H}^3\text{N}^2\text{O}^3$ . By evaporation in a vacuum over sulphuric acid, it loses 3 mols. of water, becoming  $\text{C}^6\text{H}^2\text{N}^2\text{O}^2$ , a compound isomeric with uramidobenzoic ether, into which it is converted by the application of heat.

**Carbamidodracrylic and Uramidodracrylic acids** are obtained in like manner by fusing a mixture of urea and amidodracrylic acid.

*Uramidodracrylic acid* crystallises in anhydrous, white plates, difficultly soluble even in boiling water. It is obtained with these properties, however, only when very small quantities of material are operated upon; if more than 3 grams of the two substances are fused together, the product crystallises in minute round forms which, under the microscope, have a certain resemblance to yeast-cells. All attempts to obtain the two modifications similarly crystallised have been unsuccessful; both, however, are exactly the same products of decomposition. The latter modification is also obtained by the action of potassium cyanate on amidodracrylic hydrochloride.

*Carboxamidodracrylic acid*,  $\left. \begin{array}{l} \text{C}^6\text{H}^3\text{H} \\ (\text{CO}) \\ \text{C}^6\text{H}^3\text{H} \end{array} \right\} \text{NO}^2$ , crystallises in minute needles, insoluble in all neutral solvents.

*Ortho-amidobenzoic* or *Anthranilic acid*, fused with urea, yields, not a uramido-acid, but cyananthranilic acid,  $C^6H^4(CN)NO^2$  (1st Suppl. 320):



(Griess, *loc. cit.*).

*Triamidobenzoic acid*,  $C^6H^3(NH^2)^3O^2 = C^6H^3(NH^2)^3.CO^2H$ , is produced by the action of  $4\text{in}$  and hydrochloric acid on chrysanilic (dinitro-amidobenzoic) acid. It crystallises from a hot aqueous solution in fine shining needles, which in the pure state are almost colourless, but generally have a chocolate colour. It is sparingly soluble in cold water and nearly insoluble in alcohol and ether; the solution has an acid reaction. It is resolved by heat into carbon dioxide and triamidobenzene,  $C^6H^3(NH^2)^3$ , (p. 147).

Triamidobenzoic acid combines with other acids as well as with bases. The hydrochloride  $C^6H^3(NH^2)^3.CO^2.2HCl$  is obtained by treating the liquid, after reduction, with hydrogen sulphide. It is very readily soluble in water, and crystallises in silver-grey needles; the aqueous solution undergoes decomposition on exposure to the air, with separation of brown amorphous flakes. With platinic chloride it gives, not a double salt, but a black residue; but it combines with stannous chloride, forming the compound,  $C^6H^3(NH^2)^3.CO^2.2HCl.SnCl^2 + 3\frac{1}{2}H^2O$ , which is obtained on evaporating the product of reduction, and forms monoclinic crystals. The sulphate  $C^6H^3(NH^2)^3.CO^2.H^2SO^4 + H^2O$  forms hard brownish crystals, sparingly soluble in boiling water. The nitrate  $C^6H^3(NH^2)^3.CO^2.2HNO^3$  crystallises in small rhombic six-sided brown plates, and is moderately soluble in cold water. The oxalate is obtained in fasciculated needles on mixing the hot concentrated solutions of the two acids.

The triamidobenzoates of the alkali-metals and magnesium have not been obtained in crystals. Calcium triamidobenzoate  $Ca[C^6H^3(NH^2)^3.CO^2]^2$  is obtained by neutralising the acid with calcium carbonate, and forms brown, hard crystalline crusts. Zinc triamidobenzoate  $Zn[C^6H^3(NH^2)^3.CO^2]^2 + 6H^2O$ , forms hard, light-brown shining crystals.

The aqueous solution of triamidobenzoic acid does not dissolve lead oxide, but on evaporating it with lead acetate, small shining prisms separate out, which, when once formed, are quite insoluble in water. The solution of the free acid is precipitated by copper, silver, and mercuric salts; ferric chloride produces a brown precipitate, the solution containing ferrous chloride (Salkowski, *Ann. Ch. Pharm.* clxiii. 12).

*Ethyl-amidobenzoic acid* (Griess, *Deut. Chem. Ges. Ber.* v. 1038).—When potassium amidobenzoate is treated with ethyl iodide, a mixture of ethyl- and diethyl-amidobenzoic acids is produced, which may be separated by crystallising their hydrochlorides from hot dilute hydrochloric acid.

*Ethyl-amidobenzoic acid*,  $C^6H^{11}NO^2 = C^6H^4(NH.C^2H^5)O^2$ , isomeric with the ethyl amidobenzoate,  $C^6H^5.N^2O^2$ , which Cahours obtained by reducing ethyl nitrobenzoate with ammonium sulphide, crystallises in small white or greyish prisms, slightly soluble in hot, very sparingly in cold water, but soluble in any quantity of alcohol or ether. The solutions are tasteless, but have an acid reaction. The acid melts at  $112^\circ$ , and volatilises without decomposition at a higher temperature. Like amidobenzoic acid, it unites both with bases and with mineral acids, not, however, with acetic acid. The hydrochloride,  $C^6H^{11}NO^2.HCl$ , crystallises in small four- or six-sided plates, also in needles, especially from dilute hydrochloric acid. It is moderately soluble in cold, freely in hot water, almost insoluble in cold hydrochloric acid. It forms a double salt with platinic chloride.

*Barium ethylamidobenzoate*,  $Ba(C^6H^{11}NO^2)^2 + 2H^2O$ , crystallises from water and from alcohol in small indistinct very soluble plates.

*Nitroso-ethylamidobenzoic acid*,  $C^6H^5(N \begin{Bmatrix} C^2H^5 \\ NO \end{Bmatrix})O^2$ , is formed when nitrous acid is passed into a moderately strong solution of hydrochloride of ethylamidobenzoic acid, or when potassium nitrite is added to it, and separates as a crystalline precipitate. It is sparingly soluble in boiling water, and crystallises therefrom almost completely, in yellowish-white, long, narrow plates. It is almost tasteless, but has a strong acid reaction; dissolves freely in cold alcohol and ether; and combines with bases, but not with acids. The silver salt forms small yellowish-white six-sided plates, and is but slightly soluble in boiling water.

*Diethyl-amidobenzoic acid*,  $C^{10}H^{19}NO^2 = C^6H^4(C^2H^5)^2NO^2$ , crystallises in perfectly white prisms very much like the crystals of ethyl-amidobenzoic acid, and, like the latter, has no taste, but an acid reaction; it melts at  $90^\circ$  and can be distilled without decomposition. The hydrochloride  $C^{10}H^{19}NO^2.HCl + H^2O$  forms shining four-sided plates, which are freely soluble in cold water and in hydrochloric acid, and give off their water at  $130^\circ$ .

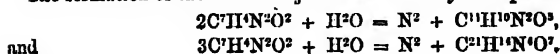
**Diallyl-amidobenzoic acid**,  $C^3H^3(C^2H^3)^2NO^2$ , is formed, as sole product, by the action of allyl iodide on potassium amidobenzoate. It crystallises in small, soft, white, plates, melting at  $90^\circ$ , sparingly soluble in boiling water, but dissolving in all proportions of alcohol or ether. The **hydrochloride**  $C^3H^3(C^2H^3)^2NO^2.HCl + H^2O$  forms large white prisms, very sparingly soluble in cold dilute hydrochloric acid; it combines with platonic chlorido.

**Diazobenzoic acid**,  $C^3H^3N^2O^2$  (Griess, *J. pr. Chem.* [2] i. 102). When the gold salt of this acid,  $C^3H^3N^2O^2.HClAuCl^3$ , suspended in alcohol, is decomposed by hydrogen sulphide, gold sulphide is precipitated, nitrogen gas is evolved, and three organic acids are formed, namely, benzoic, chlorobenzoic, and a sulphuretted acid. To obtain the latter, the filtrate from the gold sulphide is freed from alcohol by evaporation, and the residue is repeatedly boiled with a large quantity of water which does not dissolve the sulphuretted acid. On dissolving the residue in hot dilute baryta-water, evaporating, and extracting several times with hot water, the barium salt of the sulphuretted acid remains behind; it may be decomposed with ammonium carbonate, and the acid precipitated from the resulting ammonium salt by hydrochloric acid. This sulphuretted acid is nearly insoluble in water even at the boiling heat, also in cold alcohol. From a solution in boiling alcohol it separates on cooling in white needles, melting at  $242^\circ$ . It gives by analysis numbers which may be represented approximately either by  $C^3H^3SO^2$  or by  $C^3H^3S^2O^3$ , but Griess prefers the latter.

**Compounds of Diazobenzoic acid with Oxybenzoic acid** (Griess, *loc. cit.*).—1. An acid,  $C^4H^4N^2O^3 = C^3H^3O^2.C^3H^3N^2O^2$ , isomeric with azoxybenzoic acid (1st Suppl. 322), is formed, together with a brown amorphous acid and a large quantity of oxybenzoic acid, when an aqueous solution of the nitrate of diazobenzoic acid is left in contact for several days with barium or calcium carbonate. Hydrochloric acid added to the filtrate throws down a mixture of the three acids just mentioned, and on treating this mixture with cold alcohol, the acid  $C^4H^4N^2O^3$  remains undissolved. It dissolves with great difficulty in cold alcohol, but very easily in boiling alcohol and ether; water takes up only traces of it. From the hot alcoholic solution it separates in golden-yellow needles. When heated it swells up strongly and leaves a difficultly combustible cinder. Its **silver salt**  $C^4H^4Ag^2N^2O^3$  is a yellow gummy precipitate.

2. An acid having the composition  $C^4H^4N^2O^3 = C^3H^3O^2.2C^3H^3N^2O^2$  is obtained by the action of sodium carbonate on an aqueous solution of the nitrate of diazobenzoic acid for 24 hours at ordinary temperatures, and is precipitated from the resulting solution by hydrochloric acid, together with a small quantity of a brown amorphous acid, probably having the composition  $C^3H^3N^2O^3$ ; this latter may be removed by cold alcohol in which the acid  $C^4H^4N^2O^3$  is but very slightly soluble. This acid crystallises from hot alcohol in brown-red grains or short thick needles. Its ammoniacal solution, which has a deep blood-red colour, gives with silver nitrate a brown-red precipitate, having the composition  $C^4H^4Ag^2N^2O^3$ .

The formation of the two acids just described may be represented by the equations:



**Diazoxybenzoic acid**,  $C^3H^3N^2O^3 = C^3H^3 \begin{array}{c} \diagup N \diagdown \\ | \\ COOH \end{array} O$ . This acid is formed by

the action of 5 p.c. sodium-amalgam on dinitrobenzoic acid dissolved in caustic soda. The resulting black liquid neutralised with hydrochloric acid deposits a black flocculent precipitate, which when dry forms a black velvety powder, insoluble in water, alcohol, ether, benzene and acetic acid. The salts are black and amorphous, like the acid itself. The analyses of the zinc, silver, and barium salts lead to the formula of the acid above given. The acid bears a remarkable resemblance to the so-called humous or ulmous substances, which are regarded by some chemists as nitrogenous (Meyer u. Michler, *Deut. Chem. Ges. Ber.* vi. 746).

**BENZOIC CHLORIDE** or **BENZOYL CHLORIDE**,  $C^3H^3COCl$ , is strongly acted upon by sulphuric acid, with rapid evolution of hydrochloric acid, the liquid becoming sensibly warm. When an excess of sulphuric acid is used, a compound is formed which crystallises out in prisms. As soon as it is brought in contact with water, much benzoic acid separates. The crystals placed on a porous plate, a vacuum become opaque, amorphous, and completely soluble in water, with separation of benzoic acid. On adding the sulphuric acid to an excess of benzoic chloride, heating, and distilling off the excess in a current of carbonic acid, a hard, hygroscopic mass remains, which, like the preceding product, is completely

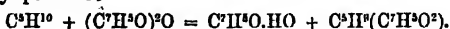


soluble in water, and consists of sulphobenzoic acid, which in this way is easily obtained in large quantity (Oppenheim, *Zeitschr. f. Chem.* [2] vii. 21).

An alcoholic solution of potassium sulphhydrate produces, by its action on benzoyl chloride, not thiobenzoic as might be expected, but principally a body indifferent to alkalis, and crystallisable from alcohol in pale red needles; this substance appears, from its properties and composition, to be identical with the benzoyl sulphide of Liebig and Wöhler (*A. Woddlgo, J. pr. Chem.* [2] iv. 50).

**BENZOIC PEROXIDE** or **BENZOYL PEROXIDE** ( $C^6H^5O$ ) $_2$ O.—For the preparation of this compound, Sperlich a. Lippmann (*Wien. Akad. Ber.* [2 Abth.] lxxii. 613), recommend the use of commercial barium peroxide, the quantity of active oxygen in which they determine by titration with iodine and sodium thiosulphate. The peroxide is triturated in a mortar with benzoyl chloride, and when the reaction is over, the product is exhausted with water, washed with dilute solution of sodium carbonate, pressed, dissolved in ether, and left to crystallise.

When an ethereal solution of benzoyl peroxide is heated to 100° with *amylene*, the ether and unaltered amylene then distilled off, and the solid residue washed with solution of sodium carbonate, a heavy oil is left which remains undecomposed even in rarefied air, and has the composition of amylene in which 1 atom of hydrogen is replaced by benzoyl peroxide:



**BENZOÏN.**  $C^{14}H^{12}O^3$  (Jena a. Limpricht, *Ann. Ch. Pharm.* clv. 89; Limpricht a. Schwanert, *Deut. Chem. Ges. Ber.* iv. 335).—This compound distilled over heated *zinc-dust* is partly or wholly deoxygenised, yielding deoxybenzoïn or toluylene oxide,  $C^{14}H^{12}O$ , toluylene  $C^{14}H^{12}$  (melting at 120°), and an oily compound isomeric with the latter, boiling at about 260°.

*Decomposition of Benzoïn by Alcoholic Potash.*—The products of this reaction vary according to the proportions of the reacting substances, the temperature and duration of the action, and the presence or absence of air.

1. When benzoïn is heated to 100° in a sealed tube for 12 hours with a small quantity of *alcoholic potash*, and the contents of the tube, after evaporation of the alcohol, are treated with water, a precipitate is formed consisting of hydrobenzoïn or toluylonic alcohol,  $C^{14}H^{12}O^2$ , and the aqueous solution treated with hydrochloric acid gives a precipitate of benzoic acid, with traces of benzilic acid.

2. When 4 grams of benzoïn are heated for two or three hours in a sealed tube to 150° with 1 gram of *sodium* dissolved in 20 c.c. alcohol of 9·2 p.c. the product treated with water as above, the liquid filtered off after twelve hours, and the undissolved portion taken up with alcohol, a solution is obtained which deposits first hydrobenzoïn, then ethyl-benzoïn,  $C^{14}H^{14}(C^2H^5)O^2$ , and lastly a compound  $C^{18}H^{24}O^4$ , which, on account of its great solubility, is difficult to separate from the last mother-liquors.

The aqueous solution mixed with hydrochloric acid gives a precipitate of ethyl-benzilic acid (p. 158).

The hydrobenzoïn obtained in the manner just mentioned is the orthorhombic modification, which forms large well-defined crystals, melting at 132°.

According to Zinin (*Deut. Chem. Ges. Ber.* vi. 1207) benzoïn is partly decomposed by boiling, or when its vapour is passed through a red-hot tube, yielding benzoic aldehyde, benzil, deoxybenzoïn, and water.

*Ethyl-benzoïn*,  $C^{14}H^{14}(C^2H^5)O^2$ , may be freed from hydrobenzoïn by repeated crystallisation. It crystallises in well-defined glassy prisms, often united in concentric groups, which dissolve easily in alcohol and ether, and melt at 95°. It is not altered by prolonged digestion of its alcoholic solution with sodium-amalgam. When it is heated with *nitric acid* of sp. gr. 1·4, and the product treated with water, a resin gradually separates, the alcoholic solution of which yields on evaporation, crystals, apparently of benzoïn, melting at 137°, and afterwards an uncrystallisable oil, which, when purified by repeated solution in cold alcohol and evaporation, and dried at 70°, exhibits the composition  $C^{14}H^{14}O^3$ , and may therefore be regarded as an isomeride of Zinin's acetyl-benzoïn  $C^{14}H^{14}(C^2H^3O)O^3$ . *Bromine* acts violently on ethyl-benzoïn, forming partly crystalline, partly oily products.

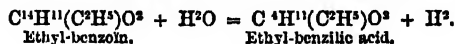
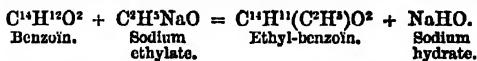
The compound  $C^{14}H^{14}O^3$  crystallises, after several days' standing at a low temperature, from the oily mother-liquor which remains after the hydrobenzoïn and ethyl-benzoïn have been removed from the precipitate formed by water; the crystals are purified by draining, pressure between paper, and recrystallisation from alcohol. It dissolves in all proportions of ether and alcohol, and separates therefrom at a low winter temperature, sometimes in well-defined crystals: it melts at 181°. Distilled

with dilute sulphuric acid, it gives off an oil which gradually solidifies, and leaves a soft yellow residue convertible, by agitation with ether and alcohol in succession, into crystals, consisting partly of a substance soluble in hot alcohol, and separating therefrom in transparent crystals melting at  $108^{\circ}$ , partly of a white crystalline powder melting at  $190^{\circ}$ , and soluble only in large quantities of alcohol. The latter has not been analysed; the former has the composition  $C^{22}H^{22}O$ , showing that sulphuric acid acts on the compound  $C^{22}H^{22}O^2$ , in the same manner as on the other members of the benzoïn group, viz. as a dehydrant.

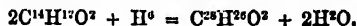
3. When benzoïn (4 parts) was heated with sodium ethylate (1 part sodium in 20 parts alcohol of 92 p. c.) to  $170^{\circ}$ , a gas, probably hydrogen, escaped on opening the tubes, and the products were somewhat different from those obtained in the experiments described under (2), toluylene  $C^4H^{12}$  being obtained instead of toluylenic alcohol  $C^4H^{14}O^2$ , (this alcohol being converted by the sodium ethylate at the high temperature of the reaction into toluylene hydrate  $C^4H^{14}O$ , benzoic acid and hydrogen, and the hydrate being then resolved into water and toluylene). The precipitate, formed by water in this case, likewise contains the compound  $C^{22}H^{22}O^2$ ; and the precipitate formed by hydrochloric acid in the aqueous solution consists of ethyl-benzilic acid, together with benzoic and very little benzilic acid.

When benzoïn is heated for three hours to  $160^{\circ}$ , with very-concentrated alcoholic potash, strong pressure shows itself on opening the tubes; water throws down toluylene and the compound  $C^{22}H^{22}O^2$ ; and hydrochloric acid added to the filtrate precipitates a large quantity of benzoic acid, with a little ethyl-benzilic, and traces of benzilic acid.

The formation of the compounds above described may be explained as follows:



The nascent hydrogen produced in this last reaction converts part of the benzoïn into toluylenic alcohol,  $C^4H^{14}O^2$ , which by the action of the alcoholic potash at high temperatures is resolved, as above mentioned into toluylene hydrate,  $C^4H^{14}O$ , benzoic acid and hydrogen, and the toluylene hydrate is in some cases further resolved into toluylene and water. The compound  $C^{22}H^{22}O^2$  is probably formed from benzoïn by the action of nascent hydrogen in the manner shown by the equation:



(Jena a. Limpricht).

4. When benzoïn is heated with alcoholic potash in an open flask, the alcohol being replaced as it evaporates, and the product is treated with water and hydrochloric acid, a resinous precipitate is formed, and the liquid after a while deposits crystals of benzoic acid containing a trace of benzilic acid. The resin freed from benzoic acid by digestion with sodium carbonate, dissolves easily in hot alcohol, forming a solution which deposits, first nodular crusts of small white crystals consisting of dibenzoïn  $C^{22}H^{22}O^2 = 2$  mols. benzoïn -  $H^2O$ , and afterwards a soft white mass the constitution of which has not been distinctly made out (Jena a. Limpricht).

According to more recent experiments by Limpricht a. Schwanert, the precipitate formed on adding water to the product obtained by several hours' digestion of benzoïn with alcoholic potash in an open vessel, consists of hydrobenzoïn (orthorhombic) and benzile (in sealed tubes no benzile is formed); and the liquid filtered from this precipitate and mixed with hydrochloric acid deposits benzoic acid, benzilic acid and ethyl-dibenzoïn,  $C^{22}H^{22}O^3 = C^{22}H^{21}(C^2H^5)O^3$ , (formerly regarded by Jena as isomeric with benzoïn, and designated as *tolane alcohol*). On boiling the precipitate formed by hydrochloric acid with water, the benzoic and benzilic acids dissolve, and ethyl-dibenzoïn remains as a resinous mass, which dissolves in alcohol and separates therefrom in crystals melting at  $200^{\circ}$ . Heated with acetyl-chloride, it is converted into acetyl-ethyl-dibenzoïn,  $C^{22}H^{22}(C^2H^5O)(C^2H^5)O^2$ .

It appears from the observations above described that the action of alcoholic potash on benzoïn gives rise to the formation of three compounds derived from two molecules of benzoïn, viz. dibenzoïn,  $C^{22}H^{22}O^2$ , ethyl-dibenzoïn,  $C^{22}H^{22}O^3$ , and the compound  $C^{22}H^{22}O^4$ .

A fourth compound, similarly derived, is oxylopidene, which Zinin obtained by the action of hydrochloric acid upon benzoïn. Dilute sulphuric acid produces the same effect:



Oxylepidene is closely allied to the compound  $C^{12}H^{12}O^2$ , and would undoubtedly be obtained from it by the action of acids. When a mixture of oxylepidene and benzoïn is heated with water to  $150^\circ$ , these bodies are converted into lepidene,  $C^{12}H^{12}O$ , and benzilo, respectively. This would account for the results obtained by Zinin, who found the two latter to be the chief products of the action of hydrochloric acid on benzoïn. (Limpricht a. Schwanert.)

**Hydrobenzoïn.**  $C^{14}H^{14}O^2$ .—It was stated in the *First Supplement*, p. 333, that the products thus designated obtained from different sources, exhibit considerable differences of melting point; and it now appears from the experiments of Ammann (*Zeitschr. f. Chem.* [2] vii. 83; *Ann. Chem. Pharm.* clxviii. 69), that there are two modifications of hydrobenzoïn, both of which are formed by the action of sodium-amalgam on benzoic aldehyde in aqueous or alcoholic solution. One of these is identical with Zinin's hydrobenzoïn, obtained by treating benzoic aldehyde with zinc and hydrochloric acid (iii. 185); the other, named isohydrobenzoïn, is the principal product of the action of sodium-amalgam on bitter-almond oil in presence of warm water; both isomerides are obtained if an alcoholic solution be used, the proportion of hydrobenzoïn rising with the strength of the alcohol employed. Their separation is very difficult, and can only be effected by repeated crystallisation from alcohol, in which isohydrobenzoïn is somewhat the more soluble.

Hydrobenzoïn crystallises from water and alcohol in anhydrous silky scales, soluble in 80 parts water at  $100^\circ$  and 400 parts water at  $15^\circ$ , easily soluble in alcohol, fusible at  $132^\circ\cdot5$ .

Isohydrobenzoïn crystallises from water in glistening hydrated needles, from alcohol in well-defined hexagonal crystals. It dissolves in 80 parts water at  $100^\circ$  and 526 parts at  $15^\circ$ , is easily soluble in alcohol, and melts at  $119^\circ\cdot5$ . It is unaltered by eight days' digestion in alcoholic solution with sodium-amalgam, and therefore seems to be not convertible into benzyl alcohol.

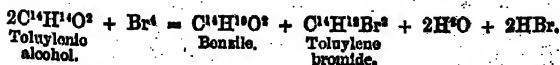
**Action of Acetyl Chloride.**—After 24 hours' digestion with acetyl chloride and expulsion of the excess by a current of air, both substances yielded products corresponding with the formula  $C^{14}H^{12}(OC^2H^3O)$ ; the isohydrobenzoïn derivative is obtained with difficulty in crystals, which melt at  $117^\circ$ – $118^\circ$ ; this substance seems to be identical with the acetic ether obtained by Limpricht and Schwanert from stilbene bromide (which melts at  $105^\circ$ – $120^\circ$ ).

**Action of Nitric Acid.**—Zinin found that hydrobenzoïn is easily converted into benzoïn by nitric acid. Isohydrobenzoïn dissolves readily in this acid; the product of the reaction collects on the surface of the liquid in oily drops, which in contact with water pass into a tough yellow mass, which could not be made to yield any definite compound.

**Action of Phosphoric Chloride.**—The reaction with isohydrobenzoïn seems to be more energetic than with hydrobenzoïn. The product of the reaction was the same with both substances, was very sparingly soluble in alcohol, and crystallised from toluene in colourless needles, melting at  $184^\circ$ , and having the composition  $C^{14}H^{12}Cl^2$ .

Limpricht a. Schwanert (*Ann. Chem. Pharm.* clx. 177), by heating toluylene bromide  $C^{14}H^{12}Br^2$  with an equivalent quantity of silver acetate mixed with glacial acetic acid for some hours in a flask with reversed condenser, obtain toluylene acetate  $C^{14}H^{12}(C^2H^3O^2)^2$ , which, when precipitated by water and heated with alcoholic potash for 24 hours, yields at least two isomeric compounds having the formula  $C^{14}H^{12}(OH)^2$ , separable by successive crystallisation from alcohol.

The least soluble of these, called toluylene alcohol, melts between  $115^\circ$  and  $146^\circ$ ; but all attempts to obtain from it a substance of constant melting point having failed, it appears most probably to consist of two mutually convertible isomerides: when heated with glacial acetic acid, acetic anhydride, or acetic chloride, it yields acetic ethers, which likewise do not exhibit any constant melting point. Nitric acid of sp. gr. 1·4 oxidises it to benzoïn, and bromine converts it chiefly into benzilo, according to the equation:



Alcoholic potash or soda at  $180^\circ$ – $200^\circ$  decomposes toluylene alcohol, with evolution of inflammable gas, yielding toluylene and oily substances which, when heated, give

off vapours having an odour of geranium. Dilute sulphuric acid abstracts the elements of water, forming a crystalline compound  $C^{14}H^{12}O$ , which melts at  $95^{\circ}$ .

Isotolulylenic alcohol crystallises in slender needles from the mother-liquors of toluylene alcohol prepared as above described; it melts at  $96^{\circ}$ , and when heated to  $160^{\circ}$  for two hours with acetic anhydride, gives two isomeric acetic ethers, melting respectively at  $135^{\circ}$  and  $96^{\circ}$ . Dilute sulphuric acid (20 p.c.) gives a small quantity of a crystalline compound,  $C^{14}H^{12}O$ , melting at  $95^{\circ}$ , and probably identical with that obtained from toluylene alcohol; the principal product, however, is an oily isomeride of this crystalline compound. Nitric acid of sp. gr. 1.4 converts isotolulylenic alcohol into benzoïn.

Limpricht a. Schwanert give the name of stilbene alcohol to the modification hitherto called hydrobenzoïn, which Zinin obtained by the action of alcoholic potash on benzoïn, reserving the name hydrobenzoïn for the other modification obtained by the action of nascent hydrogen on benzoic aldehyde (Ammann's isohydrobenzoïn). They find that stilbene alcohol crystallises in large tabular prisms melting at  $132^{\circ}$ ; heated with glacial acetic acid to  $170^{\circ}$  for two hours it furnishes the mono- and di-acetic ethers,  $C^{14}H^{12}O_2(C^2H_3O)$  and  $C^{14}H^{12}O_2(C^2H_3O)_2$ , melting respectively at  $77^{\circ}$  and  $135^{\circ}$ ; acetyl chloride and acetic anhydride give the diacetic ether melting at  $135^{\circ}$ . Bromine forms benzil and bromo-toluylene, just as with toluylene alcohol; alcoholic potash at  $180^{\circ}$  for some hours forms benzoic acid and toluylene hydrate,  $C^{14}H^{14}O$ ; this latter is further split up into water and toluylene,  $C^{14}H^{12}$ . On heating stilbene alcohol with dilute sulphuric acid for half an hour, a crystalline compound,  $C^{14}H^{14}O$ , is produced, melting at  $125^{\circ}$ .

The general conclusion deduced by Limpricht a. Schwanert from these experiments is, that toluylene bromide gives at least two isomerides of the formula  $C^{14}H^{14}O^2$ ; that benzoïn and alcoholic potash give another, with which the hydrobenzoïn of Ammann is probably identical, the isohydrobenzoïn of this chemist being probably a different isomeride. These isomerides differ in the melting point, &c., of the acetyl derivatives, and yield different bodies by the action of sulphuric acid; in some instances, however, both the toluylene and stilbene alcohols form the same products, e.g., by the action of bromine.

Ammann, on the other hand, infers from the description given by Limpricht a. Schwanert of their toluylene and isotolulylenic alcohols, that the substances so designated were not definite chemical compounds, but mere mixtures. Their melting points show that they could not be mixtures of hydrobenzoïn and isohydrobenzoïn.

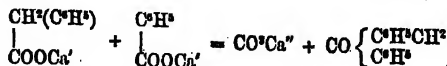
**Deoxybenzoïn or Toluylene Oxide.**  $C^{14}H^{12}O$  (Limpricht a. Schwanert, *Ann. Ch. Pharm.* clv. 59).—This compound, discovered by Zinin in 1860, was obtained by the action of zinc and hydrochloric acid on benzoïn and on benzil chloride (*1st Suppl.* 382). Limpricht a. Schwanert believed that they obtained the same compound by heating toluylene acetate with alcoholic potash, but they have since found that the compound thus obtained is not toluylene oxide  $C^{14}H^{12}O$ , but toluylene hydrate  $C^{14}H^{14}O$ .

Deoxybenzoïn is also produced when benzoïn is passed over heated zinc-dust, but the deoxidation sometimes goes further, producing toluylene  $C^{14}H^{12}$ , and an oil isomeric therewith; and, lastly, it is obtained by heating bromo-toluylene  $C^{14}H^{11}Br$  with water for several hours to  $180^{\circ}$ – $190^{\circ}$  in a sealed tube: this last appears to be the most convenient mode of preparation.

The tube after cooling is opened (strong pressure sometimes showing itself); the aqueous hydrobromic acid resulting from the action is decanted from the crystalline deoxybenzoïn; and the latter is purified by several recrystallisations from alcohol.

Deoxybenzoïn thus prepared agrees in its properties with that obtained by Zinin. It crystallises in plates sometimes of considerable size; dissolves easily in alcohol and ether, melts at  $54^{\circ}$ – $55^{\circ}$ , and may be distilled without alteration.

According to Radziszewski, deoxybenzoïn is produced by heating a mixture of benzoate and phenylacetate of calcium, whence it appears to have the constitution of phenyl-benzyl ketone:

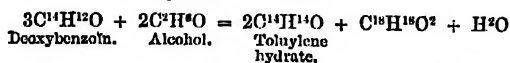
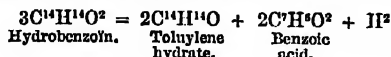


(*Deut. Chem. Ges. Ber.* vi. 489).

Deoxybenzoïn is converted, by abstraction of oxygen, into toluylene (stilbene), as when benzoïn vapour is passed over heated zinc-dust: heated to  $180^{\circ}$  for six hours with highly concentrated hydriodic acid (b. p.  $127^{\circ}$ ), it likewise yields toluylene and afterwards dibenzyl  $C^{14}H^{14}$ .

By addition of *hydrogen*, deoxybenzoin is converted into the two compounds  $C^{12}H^{12}O^2 = 2C^{11}H^{12}O + H^2$ , and  $C^{14}H^{14}O$  (toluylene hydrate) =  $C^{14}H^{12}O + H^2$ . To obtain the former of these compounds, the alcoholic solution of deoxybenzoin is heated for several hours in the water-bath with zinc-filings and hydrochloric acid, then filtered; the filtrate is mixed with water; and the precipitate, collected after twelve hours, is dissolved in alcohol. The resulting solution first deposits the compound  $(C^{12}H^{12}O^2)$  in white shining needles melting at  $156^\circ$ , and afterwards unaltered deoxybenzoin, finally leaving a viscid mother-liquor. By digesting the alcoholic solution of deoxybenzoin with sodium-amalgam for twenty-four hours in a steam-bath, filtering, neutralising the filtrate with hydrochloric acid, evaporating off the alcohol, and mixing the remaining liquid with water, a precipitate is obtained, the alcoholic solution of which first deposits the compound  $C^{12}H^{12}O^2$  in small quantity, and then toluylene hydrate  $C^{14}H^{14}O$ .

*Toluylene hydrate* is likewise formed by heating hydrobenzoin or deoxybenzoin with alcoholic potash or sodium ethylate:



and, lastly, as already observed, by heating toluylene acetate with alcoholic potash.

When, deoxybenzoin is heated in sealed tubes to  $150^\circ$  for three hours with *sodium ethylate*, (each tube containing 4 grams of deoxybenzoin and a solution of 1 gram of sodium in strong alcohol), and the contents of the tubes are mixed with water after the alcohol has been driven off by gentle heating, the liquid, after standing for some time, deposits the toluylene hydrate completely in crystals, and the filtered mother-liquor mixed with hydrochloric acid yields the compound  $C^{12}H^{12}O^2$ . If the temperature has not been allowed to rise above  $150^\circ$ , these two bodies are the only products obtained, and no pressure is exhibited on opening the tubes; but if the temperature has risen to  $160^\circ$ , slight pressure is perceptible, and if to  $170^\circ$ , a very strong pressure is exerted, and the toluylene hydrate is then for the most part resolved into toluylene and water.

Toluylene hydrate forms long, slender, glassy, brittle needles, often radiating from a common centre, very soluble in alcohol and ether, insoluble in water, melting at  $62^\circ$ , and distilling without decomposition. Nitric acid of sp. gr. 1.3 converts it into deoxybenzoin. When bromine is poured upon it, hydrobromic acid is evolved, and several compounds are formed, among which, only bromotolane  $C^{14}H^{14}Br$ , could be distinguished with certainty.

The hydrate heated with dilute sulphuric acid (1 part hydrogen sulphate to 4 parts water) is resolved into toluylene (melting at  $120^\circ$ ) and water. The same decomposition takes place, as already observed, when toluylene hydrate is heated to  $170^\circ$  with alcoholic potash; but in that case, another reaction seems also to occur, inasmuch as on opening the tube, pressure is exerted, probably resulting from hydrogen.

Toluylene hydrate dissolves very easily in acetyl chloride, forming acetyl-toluylene hydrate  $C^{14}H^{14}(C^2H^3O)O$ , which, when the excess of acetyl chloride has been expelled by gentle heating, and the hydrochloric acid by leaving the product for a week in a vacuum, is obtained as a colourless viscid liquid. The acetylated compound dissolves easily in alcohol and ether, distils for the most part undecomposed, a small portion only being resolved into acetic acid and toluylene. Heated with alcoholic potash, it is quickly resolved into acetic acid and toluylene hydrate, part of which is converted into toluylene. By heating to  $150^\circ$  for four hours with excess of acetyl chloride, it is completely resolved into acetic acid and toluylene.

The compound  $C^{14}H^{14}O^2$  is precipitated by hydrochloric acid as a resinous mass, which dissolves easily in alcohol, and either crystallises therefrom very quickly, or separates by gradual evaporation in the form of an oil, and remains in that state for weeks; it may then be made to crystallise by pouring alcohol upon it and stirring briskly. From a hot concentrated alcoholic solution it separates in tufts of long white needles; the crystals formed by slow transformation of the oil are often short transparent prisms. It melts at  $100^\circ$  (not in boiling water, but in an oil-bath heated to  $102^\circ$ - $103^\circ$ ); dissolves easily in ether and glacial acetic acid, with moderate facility in boiling, much less in cold alcohol; with yellow colour in warm strong sulphuric acid, and is reprecipitated by water. Sodium carbonate, ammonia, and caustic soda do not dissolve it, even when heated; but it dissolves in alcoholic potash, and is precipitated therefrom by hydrochloric acid, but not by water. The alcoholic solution is

not precipitated by neutral lead acetate, or silver nitrate, even on addition of ammonia; mixed with a very small quantity of potash, it gives with silver nitrate a brown precipitate of silver oxide. It is not attacked by sodium-amalgam, or when its solution in acetic acid is boiled with nitric acid. Bromine acts on the free compound and on the solution in acetic acid, forming crystalline and oily products. Heated to  $180^{\circ}$  with fuming hydrochloric acid, or boiled for two hours with dilute sulphuric acid, it forms a brown oil easily soluble in alcohol; water slowly added to the alcoholic solution throws down a brown resin, and the liquid decanted therefrom yields prismatic crystals which have likewise the composition  $C^{10}H^{10}O^2$ , but melt at  $132^{\circ}$ .

*Bromodeoxybenzoin* or *Bromotoluylene Oxide*,  $C^{11}H^{11}BrO$ , is formed by adding 1 mol. bromine to 1 mol. deoxybenzoin in ethereal solution. On distilling off the ether, a large quantity of hydrobromic acid is given off, and the oily residue solidifies after some time to a crystalline mass. The alcoholic solution of this product slowly deposits drops of oil, which on immersing the vessel in ice, are converted into white nodular crystals.

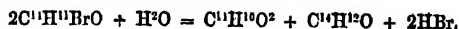
Bromodeoxybenzoin dissolves easily in ether and hot alcohol, melts at  $50^{\circ}$ , and turns yellow at  $100^{\circ}$ . When it is heated with water to  $160^{\circ}$ , or with alcoholic potash to  $150^{\circ}$ , or when its alcoholic solution is digested with sodium-amalgam or mixed with silver nitrate, the whole of the bromine is removed.

By completely precipitating the alcoholic solution with silver nitrate, removing the excess of silver with hydrochloric acid, neutralising the filtrate with sodium carbonate, evaporating, mixing the residue with water, dissolving the precipitate in alcohol, and leaving the alcoholic solution to evaporate, an oil is obtained having the composition of benzoin,  $C^{11}H^{12}O^2$ . Its formation is represented by the equation:



It does not appear, however, to be a definite compound, for after some days it deposits crystals of benzile in large quantity, leaving an oil which remains liquid for several months.

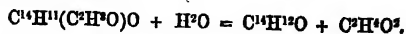
Bromodeoxybenzoin heated with water to  $160^{\circ}$  yields benzile, deoxybenzoin and hydrogen bromide:



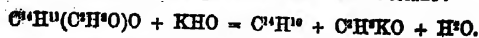
The products obtained by heating it with alcoholic potash to  $150^{\circ}$ , or by digesting its alcoholic solution with sodium-amalgam, have not been examined.

*Dibromodeoxybenzoin*  $C^{11}H^{10}Br^2O$ , analogous to chlorobenzile  $C^{11}H^{10}Cl^2O$ , is the compound which Zinin obtained by dropping bromine into fused deoxybenzoin (1st Suppl. 332). It is likewise obtained by adding bromine in excess to the ethereal solution of the latter. It crystallises in hard perfectly white prisms; dissolves easily in ether and in hot alcohol, sparingly in cold alcohol; melts at  $110^{\circ}$ - $112^{\circ}$  (at  $87^{\circ}$  according to Zinin) and turns brown at  $200^{\circ}$ . Silver nitrate added to the alcoholic solution removes all the bromine and forms benzile. Heated with water to  $160^{\circ}$ , it is completely resolved into hydrogen bromide and benzile:  $C^{11}H^{10}Br^2O + H^2O = 2HBr + C^{11}H^{10}O^2$ . On treating the alcoholic solution with hydrochloric acid and zinc, filtering after four hours, and adding water, a precipitate is obtained, the alcoholic solution of which deposits crystals of deoxybenzoin and hydrobenzoin.

*Acetyl-deoxybenzoin* or *Acetyl-toluylene Oxide*,  $C^{11}H^{11}(C^2H^3O)O$  is obtained by heating bromotoluylene  $C^{11}H^{11}Br$  (1st Suppl. 1107) to  $130^{\circ}$ - $140^{\circ}$  with silver acetate and glacial acetic. On filtering after eight hours, distilling off the greater part of the acetic acid, and adding water, a brown syrup is precipitated which separates from alcohol in the same form and shows no tendency to crystallise. It is decomposed by distillation even in a vacuum, deoxybenzoin passing over, and a considerable resinous residue being left. The acetyl-compound is slowly decomposed by water at  $200^{\circ}$ , yielding deoxybenzoin and acetic acid:



Boiled with alcoholic potash, it yields potassium acetate and tolane:



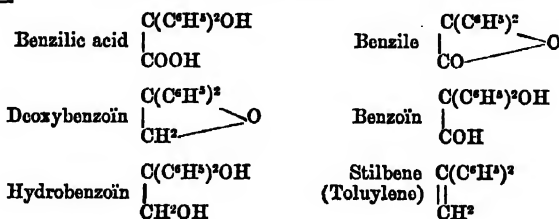
Toluylene oxides isomeric with that above described are produced by the action of dilute sulphuric acid on the several modifications of the alcohol  $C^{11}H^{12}O$ , described by Limpricht & Schwanert (p. 172). The oxide  $C^{11}H^{12}O$ , obtained in this manner from toluylalcohol, melts at  $98^{\circ}$ , and the same modification is obtained from isobenzylalcohol.

alcohol, together with another which is an oily liquid. Stilbene alcohol (Zinin's hydrobenzoïn) yields an oxide melting at 125°.

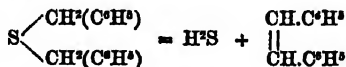
*Constitution of Benzoïn and its Derivatives.*—The constitution of these compounds has been variously represented by different chemists, the main point of discussion being whether the two phenyl-atoms contained in them are attached to the same or to different carbon-atoms. Limpricht a. Schwanert, as well as Grimaux, in 1867, proposed for deoxybenzoïn, the formula  $\begin{matrix} \text{CH.C}^6\text{H}_5 \\ \text{CH.C}^6\text{H}_5 \end{matrix} \text{O}$ , which was afterwards adopted by Kekulé in 1869. Städelér, in the same year (*Ann. Ch. Pharm.* cli. 457), proposed for this compound the formula  $\text{O} \begin{matrix} \diagup \text{C}^6\text{H}_5 \\ \diagdown \text{CH}^2 \end{matrix}$ , in which the two phenyl-atoms are attached

to the same atom of carbon; and this formula has subsequently been adopted by Limpricht a. Schwanert (*ibid.* cli. 74), in preference to their own, mainly on account of the relation of deoxybenzoïn to benzoic acid, which they regard as *diphenyl-glycollic acid*,  $\begin{matrix} \text{C}^6\text{H}_5 \\ | \\ \text{C}^6\text{H}_5 \end{matrix} \text{C}(\text{OH})_2$  (p. 158).

The formulae of the principal compounds of the series, according to this view, are as follow:—



But the formula thus assigned to stilbene is not consistent, either with its formation from the sulphides of benzyl (*1st Suppl.* 1107), or with its conversion into dibenzyl  $\text{C}^6\text{H}_5\text{—CH}^2\text{—CH}^2\text{—C}^6\text{H}_5$ , by heating with hydriodic acid. Both these reactions, indeed, lead to the formula  $\text{C}^6\text{H}_5\text{—CH=CH—C}^6\text{H}_5$  for stilbene; thus its formation from benzyl sulphide is represented by the equation:

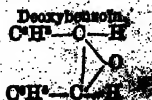
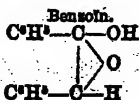
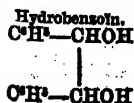


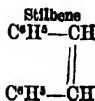
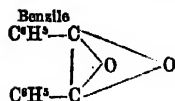
The formation of benzoïn or of hydrobenzoïn from bitter-almond oil is likewise inconsistent with Städelér's formula, inasmuch as, in so easy a transformation, it is difficult to imagine that two atoms of phenyl, originally belonging to two different molecules of bitter-almond oil, should attach themselves to the same atom of carbon.

To throw further light on this question Zincke (*Deut. Chem. Ges. Ber.* v. 836) has examined the products of oxidation of stilbene, benzoïn and benzile. Stilbene oxidised with chromic acid mixture, is converted into benzoic aldehyde and benzoic acid. The production of the former of these compounds from stilbene, regarded as  $\text{C}^6\text{H}_5\text{—CH=CH—C}^6\text{H}_5$ , is easily explained, the introduction of 2 at. oxygen splitting the molecule up into two molecules of benzoic aldehyde  $\text{C}^6\text{H}_5\text{C}^6\text{H}_4\text{O}$ , part of which is then further oxidised to benzoic acid. Benzoïn similarly treated is likewise oxidised to benzoic aldehyde and acid; also by potassium permanganate, whereas nitric acid and arsenic acid do not act upon it. Benzile is somewhat less readily oxidised than stilbene or benzoïn; but by continued heating with the oxidising mixture, it is finally converted into benzoic acid.

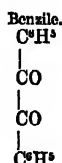
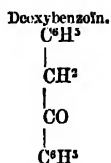
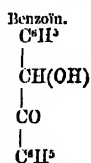
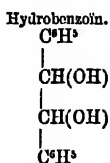
These results are likewise inconsistent with Städelér's formula, according to which the bodies above mentioned should be converted by oxidation into benzophenone or diphenyl ketone  $\text{O}(\text{C}^6\text{H}_5)_2$ .

The following formulae are regarded by Zincke as most in accordance with the known reactions and modes of formation of these bodies:—



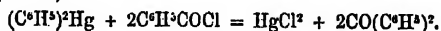


On the other hand, the mode of formation of deoxybenzoin observed by Radziszewski (p. 173), leads to the inference that this body and its congeners should be represented by ketonic formula, thus:



Hydrobenzoin and isohydrobenzoin appear to be chemically identical, inasmuch as they yield the same chloride when treated with phosphorus pentachloride (Zincke.) The modifications of hydrobenzoin and deoxybenzoin described by Limpricht a. Schwanert—supposing their existence to be established—are perhaps also merely physical modifications.

**BENZOPHENONE** or **DIPHENYL KETONE**,  $\text{C}^{12}\text{H}^{10}\text{O} = \text{CO}(\text{C}^6\text{H}_5)_2$ , may be produced by the action of benzoyl chloride on mercury-diphenyl (Otto, *J. pr. Chem.* [2] i. 144):



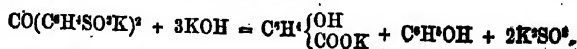
A new modification of benzophenone is obtained by the oxidation of diphenylmethane,  $\text{CH}_2(\text{C}^6\text{H}_5)_2$ . It is first obtained as an oily liquid, which, on standing in the cold, deposits large, transparent, apparently monoclinic crystals, having great resemblance to Iceland spar; they melt at  $26^\circ$ – $26.5^\circ$  to a clear liquid which boils constantly at  $300^\circ$ . The same modification of benzophenone is obtained as a by-product in the preparation of methyl-phenyl ketone. After some time the transparent crystals change their appearance; they become milk-white, and this change is accelerated by touching or gently warming them. They then melt at  $48^\circ$ – $49^\circ$ , being transformed into common rhombic benzophenone, which is the more stable form of the two (Zincke, *Deut. Chem. Ges. Ber.* iv. 576).

Benzophenone heated to  $180^\circ$  with excess of phosphorus pentachloride, forms diphenyl-dichloromethane  $\text{C}(\text{C}^6\text{H}_5)_2\text{Cl}_2$ , which, however, cannot be obtained pure, as it is decomposed by heat, and by the action of water. When freed by warming from phosphorus oxychloride, and then treated with finely divided silver, it yields tetraphenyl-ethylene  $\text{C}(\text{C}^6\text{H}_5)_4$ , which separates from solution in hot benzene in spicular crystals melting at  $221^\circ$ . (Behr, *Deut. Chem. Ges. Ber.* iii. 751).

**BENZOPHENONE-SULPHONIC ACID**,  $\text{C}^{12}\text{H}^{10}\text{SO}_3 = \text{CO} \begin{Bmatrix} \text{C}^6\text{H}_4\text{SO}_3\text{H} \\ \text{C}^6\text{H}_4\text{SO}_3\text{H} \end{Bmatrix}$ .

—Benzophenone dissolves without alteration in cold sulphuric acid and is reprecipitated by water; but if the liquid be warmed, and especially if fuming sulphuric acid be used, a sulphonic acid is formed which yields readily soluble potassium and sodium salts, and a sparingly soluble crystalline anhydrous barium salt,  $\text{CO} \begin{Bmatrix} \text{C}^6\text{H}_4\text{SO}_3 \\ \text{C}^6\text{H}_4\text{SO}_3 \end{Bmatrix} \text{Ba}$ ; a small quantity of an uncrystallisable barium salt is also formed, apparently isomeric with the crystalline salt.

The potassium salt fused with potash yields a small quantity of phenol, a large quantity of paraoxybenzoic acid, and a small quantity of a more soluble acid. The principal reaction is represented by the equation:



The formation of paraoxybenzoic acid as the principal product shows that the two groups  $\text{SO}_3\text{H}$  are in the position 1 : 4 with respect to the group  $\text{CO}$  (Städcl, *Zellulose-Chem.* [2] vii. 553).

**BENZOYL CHLORIDE**. See BENZOIC CHLORIDE, (p. 169).

**BENZOYL-BENZOIC ACID**,  $\text{C}^{14}\text{H}^{10}\text{O}_3 = \text{C}^6\text{H}_5-\text{CO}-\text{C}^6\text{H}_4-\text{CO}_2\text{H}$  (V. V.



# BENZOYL-BENZOIC ACID—BENZYL ALCOHOL. 177

Richter, *Deut. Chem. Ges. Ber.* iv. 459).—Produced by oxidising benzyl-toluene ( $\text{C}_6\text{H}_5\text{—CH}_2\text{—C}_6\text{H}_4\text{CH}_3$ ) with chromic acid, the hydrocarbon being first converted into methyl-benzophenone or tolyl-phenyl ketone  $\text{C}_6\text{H}_5\text{—CO—C}_6\text{H}_4\text{CH}_3$ , the greater part of which is then further oxidised to benzoyl-benzoic acid.

On adding an acid to a cold solution of one of its salts, the benzoyl-benzoic acid separates as a gelatinous precipitate; from a hot solution it is obtained in the form of small silky needles. It is sparingly soluble in cold water, in chloroform, benzene, and toluene, a little more in hot water; in ether, alcohol, and glacial acetic acid it dissolves readily, less easily in dilute alcohol. From hot dilute alcohol or chloroform it crystallises in thin plates having a satiny lustre; from dilute acetic acid it separates in thin long needles. It melts at  $194^\circ\text{--}195^\circ$ , and sublimes at a higher temperature in large needles very much like sublimed benzoic acid. The barium salt  $\text{Ba}(\text{C}_6\text{H}_5\text{O}_2)^2 + \text{H}_2\text{O}$  crystallises from a hot aqueous solution in ramified needles, which become anhydrous at  $160^\circ\text{--}160^\circ$ . On evaporating a saturated solution, the salt crystallises in anhydrous plates. The calcium salt  $\text{Ca}(\text{C}_6\text{H}_5\text{O}_2)^2 + 2\text{H}_2\text{O}$  crystallises in needles like the barium salt, but is more soluble. The silver salt  $\text{AgC}_6\text{H}_5\text{O}_2$  is a white precipitate, soluble in large quantities of hot water.

Benzoyl-benzoic acid is at the same time a ketone. On boiling its alcoholic solution with zinc and hydrochloric acid, it takes up hydrogen, being converted into benzhydryl-benzoic acid,  $\text{C}_6\text{H}_5\text{—CHOH—C}_6\text{H}_4\text{—CO}_2\text{H}$ , which is much more readily soluble in water and dilute alcohol than benzoylbenzoic acid. It crystallises in ramified needles, melts at  $164^\circ\text{--}165^\circ$ , and is decomposed at a higher temperature. By oxidising agents it is easily reconverted into benzoyl-benzoic acid. The barium salt  $\text{Ba}(\text{C}_6\text{H}_5\text{O}_2)^2$  forms long hard needles grouped in stars; the calcium salt  $\text{Ca}(\text{C}_6\text{H}_5\text{O}_2)^2 + 3\text{H}_2\text{O}$  crystallises in white needles resembling wavelite. The silver salt  $\text{AgC}_6\text{H}_5\text{O}_2$  is a white precipitate sparingly soluble in boiling water.

Benzhydrylbenzoic acid has the same composition as benzoic acid, but these two acids are not identical.

When benzhydryl-benzoic acid is heated with concentrated hydriodic acid to  $150^\circ$  for some hours, it is transformed into benzyl-benzoic acid,  $\text{C}_6\text{H}_5\text{—CH}_2\text{—C}_6\text{H}_4\text{—CO}_2\text{H}$ , which is also obtained, besides other products, by acting on the hydrocarbon with dilute nitric acid. This acid is sparingly soluble in cold water; from a hot solution it crystallises in microscopic needles; from dilute alcohol in larger needles or plates with a satiny lustre. It melts at  $154^\circ\text{--}155^\circ$ , and sublimes like benzoyl-benzoic acid.

The barium salt  $\text{Ba}(\text{C}_6\text{H}_5\text{O}_2)^2$  is sparingly soluble, and forms crystalline crusts. The calcium salt  $\text{Ca}(\text{C}_6\text{H}_5\text{O}_2)^2$  has similar properties, and the silver salt is a white precipitate. By oxidising agents it is reconverted into benzoylbenzoic acid. On subjecting the calcium salt to distillation, diphenylmethane is produced.

**BENZOYL-SULPHONIC ACID.**  $\text{C}_6\text{H}_5\text{SO}_3\text{H} = \text{C}_6\text{H}_5\text{—CO—SO}_3\text{H}$ .—This acid, isomeric with sulphobenzoic acid, is obtained by the action of sulphuric acid in excess on benzoyl chloride. It crystallises in prisms, and is decomposed by water, yielding a large quantity of benzoic acid. By keeping, and more quickly by heating, it is converted into sulphobenzoic acid, which may accordingly be conveniently prepared by heating benzoyl chloride with excess of sulphuric acid (Oppenheim, *Deut. Chem. Ges. Ber.* iii. 735).

**BENZYL**, or **DIBENZYL**,  $\text{C}_6\text{H}_5\text{CH}_2$ , passed in the state of vapour through red-hot tubes three feet long filled with pumice, is resolved into toluene and toluylene (stilbene),  $2\text{C}_6\text{H}_5\text{CH}_2 = 2\text{C}_6\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_5\text{CH=CH}_2$  (Otto & Dreher, *Ann. Ch. Pharm.* cliv. 176).

Stilbene is also formed in considerable quantity, together with another hydrocarbon not yet isolated, when dibenzyl vapour is passed over heated lead oxide (Behr & van Dorp, *Deut. Chem. Ges. Ber.* vi. 753).

**BENZYL ALCOHOL.**  $\text{C}_6\text{H}_5\text{CH}_2\text{OH} = \text{C}_6\text{H}_5\text{CH}_2\text{OH}$ .—Kachler (*J. pr. Chem.* cvii. 307) prepares this alcohol from Peru balsam by the following process:—This balsam, which consists essentially of benzyl cinnamate, together with cinnamic acid and resins, is shaken with twice its volume of concentrated alcoholic potash (whereupon potassium benzoate separates), then with warm water, and the separated oil is heated with four times its volume of aqueous potash of sp. gr. 1.3, till the layers previously separated have dissolved to a clear liquid. The crystals which separate on cooling are pressed, and the liquid is diluted and boiled, whereupon the benzyl alcohol passes over.

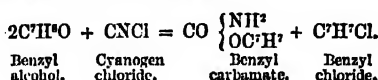
Benzyl alcohol may also be obtained from liquid storax. By saponifying the crude styracine (chiefly cinnyl cinnamate) obtained from this resin, a product is obtained which begins to boil a little above  $100^\circ$ , and yields by fractional distillation benzyl

alcohol, boiling at 205°–207°, xylol alcohol  $C^{10}H^{10}O$  boiling at 217°, and other products (Laubenheimer, *Ann. Ch. Pharm.* clxiv. 289). See STORAX.

**Action of Cyanogen Chloride on Benzyl Alcohol.**—When gaseous cyanogen chloride liquefied by cooling, is mixed in tubes drawn out in the middle (for convenience of sealing) and immersed in a freezing mixture with benzylic alcohol, in the proportion of  $CNCl$  to  $2C^6H^5O$ , and the tubes, after being sealed, are exposed for an hour or two to the temperature of the air, the contents become hot and acquire a yellowish colour, and, on subsequent cooling, solidify to a crystalline mass, mixed in the lower parts with a small quantity of white amorphous substance. If the tubes be then opened (after again immersing them in the freezing mixture to prevent loss from projection) and the contents, liquefied by gentle warming, are poured into a flask and distilled under a pressure of about 10 mm., first in the water-bath and finally in a bath of salt water, benzyl chloride passes over, and the residue solidifies to a crystalline mass containing benzyl carbamate, which may be purified by repeated crystallisation from ether till it dissolves completely therein, and finally by crystallisation from boiling water. The matter insoluble in ether (the white amorphous substance above mentioned), consists of sal-ammoniac, and an organic substance insoluble in water, alcohol, and ether, slightly soluble in carbon sulphide.

If an excess of cyanogen chloride be added, the reaction takes place in the same way, the excess partly remaining unaltered, and being partly converted into solid cyanogen chloride; a small quantity of hydrochloric acid is also frequently evolved.

The principal and final action of gaseous cyanogen chloride on benzyl alcohol may therefore be represented by the following equation:—



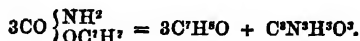
The same products are obtained with solid cyanogen chloride. When this substance is triturated in a mortar with benzyl alcohol, added drop by drop till the proportion amounts to  $C^6H^5Cl$  to  $6C^6H^5O$ , the reaction commences with evolution of heat, a small quantity of hydrochloric acid being given off before the whole of the benzyl alcohol has been added; and on placing the mortar, after the reaction is terminated, in a steam-bath, decanting the liquid portion of the contents into a flask, and distilling as above, benzyl chloride passes over and benzyl carbamate remains behind. The solid residue in the mortar yields to ether another portion of the carbamate, and the portion insoluble in ether contains sal-ammoniac, together with a white substance slightly soluble in boiling water, crystallising therefrom in gelatinous flocks, and very similar in appearance to the substance which Habich obtained in preparing cyanuric acid by heating urea.

Solid cyanogen chloride heated with benzyl alcohol to higher temperatures (180°–200°) yields, in addition to benzyl chloride and sal-ammoniac, two crystalline substances and scarcely a trace of benzylic carbamate. By repeated crystallisation from alcohol and ether, these two bodies are obtained, the one in slender, flexible, dazzling-white needles, melting at about 153°, and having nearly the composition of benzyl cyanate or cyanurate; the other in hard yellowish prisms, melting at about 143°, and containing about 75–76 p.c. carbon, 6.1 hydrogen, and 11.2 nitrogen, a composition agreeing approximately with the formula  $C^{12}H^{14}N^2O$ . This latter substance, treated with potash, yields a liquid base resembling dibenzylamine in odour and appearance (Cannizzaro, *Gazzetta chimica italiana*, i. 33).

**Action of Urea Nitrate.** The products of this reaction vary according to the temperature. When the two substances are heated together in a water-bath, or to any temperature below 120°, the chief products are dibenzylurea,  $CH^2(C^6H^5)^2N^2O$ —identical with that which Cannizzaro obtained by the action of potassium cyanate on benzyl chloride—and benzoic aldehyde; but when the temperature of the mixture is raised to 130°–140°, the chief product is benzyl carbamate, together with a small quantity of another substance insoluble in cold ether, soluble in very strong alcohol and in boiling ether, from which it separates in crystals melting at 151°–153°. This process cannot, however, be recommended for the preparation either of dibenzylurea or of benzyl carbamate, as the product in either case is but small in proportion to the quantity of benzyl alcohol consumed (Campisi e. Amato, *Gazzetta chimica italiana*, i. 39).

**BENZYL CARBAMATE or BENZYL-URETHANE.**  $C^6H^5N^2O$  =  $CO \begin{Bmatrix} NH^2 \\ OC^6H^5 \end{Bmatrix}$ .—This compound, whether prepared with gaseous or with solid cyanogen

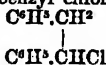
chloride, crystallises in beautiful transparent colourless laminae, melting at 86°, moderately soluble in warm water, from which it crystallises on cooling, more soluble in ether, extremely soluble in alcohol. When it is heated in a retort to 200°-230°, a very small portion sublimes unaltered, but the greater part is resolved into benzyl alcohol and cyanuric acid:



(Cannizzaro, *loc. cit.*)

**BENZYL CHLORIDE.**  $\text{C}^2\text{H}^2\text{Cl} = \text{C}^2\text{H}^2.\text{CH}^2\text{Cl}$ .—This compound, heated in a sealed tube with sodium thiosulphate, yields a thick brownish oil, which contains a large quantity of sulphur, smells faintly of bitter-almond oil, and when distilled, gives off hydrogen sulphide, small quantities of benzyl sulphhydrate, and toluene, but chiefly toluylene (stilbene). On raising it to a very high temperature, thionessal and tolyl-allyl sulphido distil over. Now as these products are formed by the decomposition of the sulphide and sulphhydrate of benzyl (1st Suppl. 1087), it may be inferred that these latter compounds are the primary products of the action of sodium thiosulphate on benzyl chloride (R. Otto, *Zeitschr. f. Chem.* vi. 26).

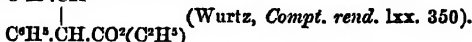
Benzyl chloride heated with ethylic chlorocarbonate and sodium-amalgam is converted into dibenzyl-carbonylic acid  $\text{C}^2\text{H}^2\text{O}^2$ . The reaction apparently takes place by two stages, two molecules of benzyl chloride uniting together, with elimination of  $\text{HCl}$ , to form chloro-dibenzyl



and this compound being converted by the joint action of the sodium and the chlorocarbonic ether into ethylic



dibenzylcarbonylate



(Wurtz, *Compt. rend.* lxx. 350).

**BENZYL CYANIDE, DERIVATIVES OF.** (Czampilek, *Deut. Chem. Ges. Ber.* iii. 472). *Nitrobenzyl Cyanide*,  $\text{C}^2\text{H}^2\text{NO}^2 = \text{C}^2\text{H}^2(\text{NO}^2).\text{CH}^2\text{CN}$ .—This compound is produced by dropping benzyl cyanide (prepared by repeatedly distilling benzyl chloride with alcoholic potassium cyanide) into fuming nitric acid contained in a cooled vessel. On leaving the liquid to stand over-night, and then pouring it into water, the nitro-compound separates as an oily body, which soon solidifies in crystals; it may be purified by washing it, first with water, then on a filter with cold alcohol, and dissolving it in boiling alcohol, whence it crystallises on cooling in long needles, which turn red in an alcoholic solution of potash or soda, the colour being changed to green by acids.

*Amidobenzyl Cyanide*,  $\text{C}^2\text{H}^2\text{N}^2 = \text{C}^2\text{H}^2(\text{NH}^2).\text{CH}^2\text{CN}$ , is obtained as a hydrochloride by treating the nitro-cyanide with tin and hydrochloric acid, decomposing the resulting tin-compound with hydrogen sulphide, and concentrating the filtered liquid. The hydrochloride  $\text{C}^2\text{H}^2\text{N}^2.\text{HCl}$  then separates in beautiful tablets, sparingly soluble in cold, more soluble in hot alcohol. The *platino-chloride* has the composition  $2(\text{C}^2\text{H}^2\text{N}^2.\text{HCl}).\text{PtCl}_4$ . The base  $\text{C}^2\text{H}^2\text{N}^2$ , obtained by decomposing the hydrochloride with soda-loy, agitating with ether, and evaporating, forms concentric groups of scaly crystals; from water it separates as an oil.

The corresponding *azo-compound* appears to be formed by treating nitrobenzyl cyanide dissolved in absolute alcohol with sodium-amalgam; the liquid turns red, and after a while acquires a fine blue colour.

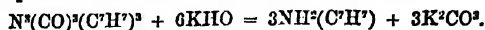
**BENZYL IODIDE**,  $\text{C}^2\text{H}^2.\text{CH}^2\text{I}$ .—Produced by the prolonged action of hydriodic acid of sp. gr. 1.96 on benzyl chloride at ordinary temperatures; at 120°-140°, the product consists of toluene and oils boiling above 280°. The iodide forms colourless crystals, having at 25° a sp. gr. of 1.7336, compared with water at the same temperature; it melts at 24.1°, contracts in solidifying, does not volatilise without decomposition. It is soluble in ether, carbon sulphide, and alcohol (slightly at 0°), insoluble in water. Its vapour excites tears. By silver acetate at ordinary temperatures it is immediately converted into benzyl acetate, and with alcoholic ammonia it quickly yields crystals of tribenzylamine (melting at 92°), while the hydriodides of mono- and dibenzylamine remain in solution (Lieben, *Zeitschr. f. Chem.* [2] vi. 786).

**BENZYL ISOCYANATE and ISOCYANURATE**,  $\text{N}\left\{\begin{array}{c}(\text{CO})^2 \\ \text{C}^2\text{H}^2\end{array}\right.$  and  $\text{N}\left\{\begin{array}{c}(\text{CO})^2 \\ (\text{C}^2\text{H}^2)^2\end{array}\right.$  (Letts, *Chem. Soc. J.* [2] x. 446). These ethers are produced by the action of silver cyanate on benzyl chloride. On heating these substances together in a paraffin-bath, the isocyanate distils over as a colourless transparent liquid; and, on heating the

remainder over a naked flame, the isocyanurate passes over as a yellowish oily liquid, which solidifies, on cooling, to a hard crystalline mass.

The isocyanurate has an excessively pungent odour, and its vapour causes the eyes to smart painfully. It boils between  $175^{\circ}$  and  $200^{\circ}$ , but cannot be completely freed by distillation from benzyl chloride, which boils at  $175^{\circ}$ . Alcoholic ammonia converts the isocyanate into benzyl-urea.

The isocyanurate  $N^*(CO)^2(C^6H^5)^3$  is the chief product of the reaction above mentioned. It dissolves slowly in hot alcohol, and separates on cooling in beautiful light silky needles. It is insoluble in water; dissolves with difficulty in ether, more readily in alcohol; melts at  $157^{\circ}$ , and boils at a temperature above  $320^{\circ}$ . By repeated sublimation in a tube, it is converted into the isocyanate; when fused with caustic potash, it yields potassium carbonate and benzylamine:

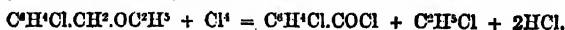


The solid substance melting at about  $153^{\circ}$ , which Cannizzaro obtained, as above mentioned, among the products of the action of solid cyanogen chloride on benzyl alcohol, was perhaps also the isocyanurate.

#### BENZYL KETONES. See KETONES.

#### BENZYL OXYGEN-ETHERS. (Sintenis, *Deut. Chem. Ges. Ber.* iv. 909).

—These ethers treated with chlorine or bromine are decomposed, without formation of substitution-products. *Benzyl-methyl oxide*  $C^6H^5.CH^2.OCH^3$  and *benzyl-ethyl oxide*  $C^6H^5.CH^2.OCH^2H^3$ , treated with dry chlorine in the cold, yield benzoic aldehyde, hydrochloric acid, and chloride of methyl or ethyl; and *chlorobenzyl-ethyl oxide*  $C^6H^4Cl.OCH^2H^3$  is decomposed into chlorobenzoic aldehyde,  $C^6H^3ClO$ , and ethyl chloride. By the action of chlorine at the boiling heat, the methyl and ethyl ethers yield methyl or ethyl chloride and benzoyl chloride, and chlorobenzyl-ethyl oxide splits up into chlorobenzoyl chloride and ethyl chloride:



When benzyl-ethyl oxide is acted upon by chlorine in presence of iodine, the products are ethyl iodide and monochlorobenzoyl chloride, which by oxidation is converted into parachlorobenzoic acid.

*Benzyl-phenyl oxide*,  $C^6H^5.CH^2.OCH^2C^6H^5$ , prepared by heating an alcoholic solution of benzyl chloride with potassium phenate, is also decomposed by chlorine or bromine, which, when acting in the cold, yield trichlorophenol or tribromophenol and benzyl chloride or bromide. As a similar decomposition takes place when only one molecule of chlorine or bromine is used, it is obvious that, in the first stage of the reaction, a substituted ether is formed, which is further decomposed by the hydracid produced, just as the anisols are split up by the action of hydriodic acid; and indeed by heating benzyl-phenyl oxide with hydrochloric acid to  $100^{\circ}$ , benzyl chloride and phenol were formed.

To obtain substitution-products, it is therefore necessary to remove the acid as soon as it is formed, which is easily effected by adding mercuric oxide. By adding bromine to an alcoholic solution of the ether in which freshly precipitated mercuric oxide is suspended, benzyl-bromophenyl oxide  $C^6H^5.CH^2.OCH^2C^6H^4Br$  is formed. This compound crystallises from alcohol in long white needles melting at  $59^{\circ}$ – $59.5^{\circ}$ ; it is not acted upon by caustic soda-solution. By the action of chlorine under the same conditions, the chlorinated ether,  $C^6H^5.CH^2.OCH^2C^6H^4Cl$ , is obtained, which forms long needles melting at  $71^{\circ}$ – $71.5^{\circ}$ .

#### BENZYL SULPHOCYANATE, $C^6H^5NS = S \begin{Bmatrix} CN \\ C^6H^5 \end{Bmatrix}$ ; metameric with benzyl-

sulphocarbimide  $N \begin{Bmatrix} CS \\ C^6H^5 \end{Bmatrix}$  (1st Suppl. 1056), is formed by heating benzyl chloride with the equivalent quantity of potassium sulphocyanate in presence of alcohol in a retort with reversed condenser. When recrystallised from alcohol, it forms large transparent prisms, insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol, easily soluble also in ether and in carbon sulphide. It has a pungent taste and smell, melts at  $36^{\circ}$ – $38^{\circ}$ , and boils, with partial decomposition at  $256^{\circ}$  (benzyl-sulphocarbimide boils at  $243^{\circ}$ ). It unites rapidly with dry gaseous hydrogen bromide, forming a crystallised compound, insoluble in ether and instantly decomposed by water.

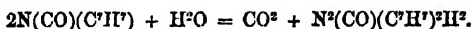
Fuming nitric acid converts it into *nitrobenzyl sulphocyanate*,  $S \begin{Bmatrix} CN \\ C^6H^4(NO^2) \end{Bmatrix}$ . The same compound is formed by heating nitrobenzyl chloride  $C^6H^4(NO^2)Cl$  with potassium sulphocyanate in the manner above described. It crystallises from alcohol

solution in small brittle needles, which volatilise at about  $70^{\circ}$ , but decompose when heated before they distil (L. Henry, *Zeitschr. f. Chem.* vi. 207).

**BENZYL UREAS.** (Cannizzaro, *Gazzetta chimica italiana*, ii. 41.—Letts, *Chem. Soc. J.* [2] x. 449). *Monobenzyl-urea*  $\text{CH}_2(\text{C}^6\text{H}_5)\text{N}^{\text{H}}\text{O}$  and *Dibenzyl-urea*  $\text{CH}_2(\text{C}^6\text{H}_5)_2\text{N}^{\text{H}}\text{O}$  are produced simultaneously when benzyl chloride and potassium cyanate in alcoholic solution are continuously heated in an apparatus with reversed condenser.

On distilling off the alcohol and treating the residue with boiling water, an oily substance separates, which, on cooling, solidifies to a crystalline mass containing dibenzyl-urea. The aqueous solution contains the potassium chloride formed in the reaction, the carbonate resulting from decomposition of the cyanate, and monobenzyl-urea; and on evaporating this solution to dryness over the water-bath, treating the residue with a large quantity of ether, and distilling off the ether, the monobenzyl-urea remains behind, and may be purified, by recrystallisation, either from water or from alcohol. The two benzyl-ureas may likewise be obtained with tolerable facility by heating urea, benzyl chloride, and alcohol together in an apparatus with reversed condenser, then distilling off the alcohol, and treating the residue with water. The dibenzyl-urea is contained in the oily insoluble portion of the product, while the monobenzyl-urea dissolves in the water, and may be separated and purified as above (Cannizzaro).

Monobenzyl-urea is also produced by the action of alcoholic ammonia on benzyl isocyanate, and dibenzyl-urea by heating the same compound to  $100^{\circ}$  with water in a sealed tube (Letts):



Monobenzyl-urea crystallises in long white needles moderately soluble in water and in alcohol, more soluble at high than at low temperatures, freely soluble in ether. It melts at  $147^{\circ}$ – $147.5^{\circ}$ , but begins at the same time to give off ammonia, and after being once fused, melts at a lower temperature (Cannizzaro). According to Letts, it melts at  $144^{\circ}$ . Heated to about  $200^{\circ}$ , it slowly gives off ammonia, and yields a white sublimate, which crystallises from alcohol in white needles having the appearance, composition and melting point of dibenzyl-urea (Cannizzaro).

Dibenzyl-urea is insoluble in water, but dissolves very easily in alcohol, from which it crystallises in beautiful white needles, melting at  $167^{\circ}$ . Both dibenzyl- and monobenzyl-urea form crystalline platinumchlorides, but no solid compounds with nitric or hydrochloric acid (Letts).

*Phenyl-benzyl-urea*,  $\text{CH}_2(\text{C}^6\text{H}_5)(\text{C}^6\text{H}_5)\text{N}^{\text{H}}\text{O}$ .—A mixture of benzyl isocyanate and aniline becomes hot and solidifies on cooling to a brown crystalline mass of phenyl-benzyl-urea, which, when purified by recrystallisation from alcohol, forms white needles melting at  $168^{\circ}$ . This compound is insoluble in water, and in hydrochloric acid, and forms an insoluble platinum salt, but not a crystallisable nitrate. When heated, it gives off pungent fumes of benzyl isocyanate (Letts).

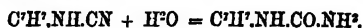
**BENZYLAMINE**,  $\text{C}^6\text{H}_5\text{N} = \text{C}^6\text{H}_5\text{CH}_2\text{NH}_2$ . (Strakosch, *Deut. Chem. Ges. Ber.* v. 692).—The decomposition of isocyanate or isocyanurate of benzyl (p. 180) with potash, affords the means of preparing this base more readily than by the former method of heating benzyl chloride with alcoholic ammonia (1st Suppl. 336). The product obtained by heating benzyl chloride with silver cyanate is distilled, and the distillate, consisting of a mixture of the isocyanate and isocyanurate, is digested with caustic potash and subjected to distillation. The product generally contains some di- and tri-benzylamine, owing to the presence of undecomposed benzyl chloride. To purify it, the distillate is treated with hot hydrochloric acid; tri-benzylamine hydrochloride then remains undissolved, while the dibenzylamine salt soon crystallises out. The solution is then decomposed by caustic potash, and the base dried over solid potash. Benzylamine boils constantly at  $185^{\circ}$ .

#### Derivatives of Benzylamine.

*Cyanbenzylamine*,  $(\text{C}^6\text{H}_5\text{NH})_2(\text{CN})$ , is produced by passing cyanogen-gas into a cold solution of benzylamine. When recrystallised from alcohol, it forms colourless, shining crystals melting at  $140^{\circ}$ . It is insoluble in water, but dissolves in alcohol and ether. The hydrochloride  $(\text{C}^6\text{H}_5\text{NH})_2(\text{CN}) \cdot 2\text{HCl}$  crystallises in white silky needles soluble in water and alcohol, and forms a crystalline platinum compound. Cyanbenzylamine, heated for some time with hydrochloric acid, is converted into benzylloxamide, dibenzylloxamide, and, on continued heating, even into oxamide.

*Dibenzylamide*,  $\text{CO.N(C}^6\text{H}_5\text{)}_2\text{H}$ , may also be obtained by boiling benzylamine with oxalic ether. It crystallises from boiling alcohol in white silky scales, dissolving sparingly in hot alcohol, but not in water and ether; it melts at  $216^\circ$ .

*Cyanbenzylamide*,  $\text{C}^6\text{H}_5\text{.NH.CN}$ , is obtained by passing dry cyanogen chloride into a cold ethereal solution of anhydrous benzylamine. The saturated solution is filtered from the benzylamine hydrochloride, the ether evaporated, and the residue placed in a vacuum. When recrystallised from ether, it forms transparent plates melting at  $33^\circ$ ; it is readily soluble in alcohol and ether, but insoluble in water. It does not combine with hydrochloric acid; on boiling it with this acid or with water, it is converted into monobenzyl-urea:



*Tribenzylmelamine* or *Tricyantribenzyltriamine*,  $(\text{C}^6\text{H}_5)_3(\text{NH})_3(\text{CN})_3$ .—Cyanbenzylamide soon undergoes polymerisation, even when kept in closed vessels or in a vacuum; the crystals melt, forming a heavy liquid which after some time becomes viscid, and at last solidifies; this transformation takes place more quickly on a water-bath. On treating the product with hydrochloric acid, the hydrochloride,  $(\text{C}^6\text{H}_5)_3(\text{NH})_3(\text{CN})_3.2\text{HCl}$ , is formed, which is sparingly soluble in water, more freely in alcohol and ether, and crystallises in needles. The free base obtained by decomposing this salt, dissolves in water and alcohol, crystallises in laminae, melts at a much higher temperature than cyanbenzylamide, and forms a platino-chloride.

*Dibenzylguanidine*,  $\text{C} \begin{Bmatrix} \text{NH.C}^6\text{H}_5 \\ \text{NH} \\ \text{NH.C}^6\text{H}_5 \end{Bmatrix}$ .—The hydrochloride of this base is produced by boiling an alcoholic solution of cyanbenzylamide and benzylamine hydrochloride, and the free base is formed by the action of dry cyanogen chloride upon pure dry benzylamine. The hydrochloride crystallises in laminae, melting at  $176^\circ$ , and dissolving sparingly in water, more readily in alcohol; with platinic chloride it forms a crystalline double-salt. By adding soda-solution to a solution of the hydrochloride the base is precipitated as an oil which soon solidifies, and crystallises from alcohol in colourless laminae or plates, melting at  $100^\circ$ , and dissolving freely in water, alcohol, and ether.

*Dibenzyl Sulpho-urea*,  $\text{CS} \begin{Bmatrix} \text{NH.C}^6\text{H}_5 \\ \text{NH.C}^6\text{H}_5 \end{Bmatrix}$ .—An alcoholic solution of benzylamine is heated in a flask connected with a reversed condenser as long as hydrogen sulphide is given off. The product is evaporated and the residue crystallised repeatedly from alcohol. It forms large four-sided brilliant plates, melting at  $114^\circ$ , and dissolving in alcohol and ether, but not in water. On heating it with mercuric oxide, it is converted into dibenzyl-urea.

*Benzylacetamide*,  $\text{C}^6\text{H}_5\text{.C}^6\text{H}_5\text{O.HN}$ , is formed when anhydrous acetic acid and benzylamine are heated together for some hours. It forms radiate needles, melting at  $30^\circ$ , boiling above  $250^\circ$ , and having a pleasant odour like that of flowers. It is very freely soluble in alcohol and ether, and does not crystallise from these solutions. It is remarkably stable, not being acted upon by acids, and not deprived of its acetyl by treatment with potash. By nitric acid it is converted into nitrobenzylacetamide, which crystallises from ether in yellow deliquescent needles or laminae. From this compound, too, the acetyl-group cannot be removed without complete destruction.

*Nitrobenzyl mercaptan*,  $\text{C}^6\text{H}_4(\text{NO}_2)\text{CH}_2\text{SH}$ , is formed by treating nitrobenzyl chloride with alcoholic ammonium sulphide. It forms small colourless, shining, plates, melting at  $140^\circ$ , insoluble in water, but soluble in alcohol and ether. The same compound is formed by boiling nitrobenzyl chloride with potassium sulphhydrate. By the continued action of ammonium sulphide or ammonia on this mercaptan, nitrobenzyl disulphide,  $\text{C}^6\text{H}_4(\text{NO}_2)\text{CH}_2\text{S}$ , is produced, in yellow microscopic crystals, melting at  $89^\circ$ ; it is insoluble in water, but dissolves in alcohol and ether.

When nitrobenzyl chloride is heated with alcoholic ammonia in a sealed tube, a mixture of different bases is produced, including nitrotribenzylamine, the hydrochloride of which is insoluble in water and sparingly soluble in alcohol (Strakosch).

**BENZYL-BENZENE**,  $\text{C}^{12}\text{H}_{12} = \text{C}^6\text{H}_4(\text{C}^6\text{H}_5) = \text{C}^6\text{H}_5\text{—CH=CH}^6\text{H}_5$ . (Zincke, *Deut. Chem. Ges. Ber.* iv. 298; *Chem. Soc. J.* [2] ix. 508, 688).—This hydrocarbon, which has the constitution of diphenyl-methane, is formed, together with other

products, when benzyl chloride is heated with benzene and zinc-dust. It constitutes the lower-boiling portion of the distillate, and solidifies on cooling to a crystalline mass of prismatic needles melting at  $21^{\circ}$ – $25^{\circ}$ ; by slow cooling, large fine tables are sometimes formed. It dissolves readily in strong nitric acid, forming a crystalline nitro-product, and is slowly oxidised by a boiling mixture of dilute sulphuric acid and potassium dichromate, yielding a small quantity of benzoic acid and benzophenone  $\text{C}^6\text{H}_5\text{—CO—C}^6\text{H}_5$ , identical with that obtained from calcium benzoate. These reactions indicate the constitution of the compound; it is probably identical with the *diphenylated marsh-gas* which Jena obtained by distilling barium diphenylacetate with soda-lime (*Ann. Ch. Pharm.* civ. 86).

By using toluene, xylene, &c., in place of benzene in the above reaction, homologues of benzyl-benzene, represented by the general formula,  $\text{C}^n\text{H}^{2n-14}$ , may be obtained. Reduced iron or finely divided copper may be used in place of zinc-dust; with copper, however, a higher temperature is required.

**Benzyl-toluene**,  $\text{C}^{11}\text{H}^{14}$  or probably  $\text{C}^6\text{H}_5\text{—CH}_2\text{—C}^6\text{H}_4\text{—CH}_3$  (Zincke, *Deut. Chem. Ges. Ber.* iv. 298; v. 683), isomeric with dibenzyl and ditolyl, is formed by heating a mixture of benzyl chloride and toluene with zinc-dust or reduced iron. It is a colourless oil, which boils at  $277^{\circ}$ , and when boiled with chromic acid mixture yields benzoyl-benzoic acid  $\text{C}^{11}\text{H}^{10}\text{O}_3$  (p. 177).

Vapour of benzyl-toluene passed over heated lead oxide yields a considerable quantity of anthracene (Behr and van Drop, *Deut. Chem. Ges. Ber.* vi. 753).

Benzyl-toluene is violently acted upon by *bromine*, even when dissolved in carbon bisulphide, but it has not been found possible to isolate a definite compound from the product.

**Nitrobenzyl-toluenes**.—Concentrated nitric acid converts benzyl-toluene into dinitrobenzyltoluene  $\text{C}^{11}\text{H}^{12}(\text{NO}_2)_2$ , a large quantity of a resinous body being formed at the same time. The dinitro-compound crystallises from hot alcohol in slender white needles, or on slowly cooling in thin prisms, and by spontaneous evaporation of the solution it is obtained in brilliant prisms melting at  $137^{\circ}$ . If instead of concentrated nitric acid, an acid of sp. gr. 1.4 is used, the action begins only at the heat of the water-bath; nitrous fumes are evolved, and besides nitration, oxidation also takes place, the chief product having the composition  $\text{C}^{11}\text{H}^{11}(\text{NO}_2)_3$ , probably nitro-methylbenzophenone  $\text{C}^6\text{H}_4(\text{NO}_2)\text{—CO—C}^6\text{H}_4\text{—CH}_3$ . It crystallises from hot dilute alcohol in long flat needles, or silky plates, melting at  $127^{\circ}$ , and subliming without decomposition in shining plates. When treated with tin and hydrochloric acid, it yields an amido-compound, forming amorphous salts, from which it is precipitated by soda-solution as a light white powder (Zincke). Tetranitrobenzyltoluene,  $\text{C}^{11}\text{H}^{10}(\text{NO}_2)_4$ , is obtained, together with resinous bodies, by acting on the hydrocarbon with a mixture of highly concentrated nitric acid and concentrated sulphuric acid. It crystallises from hot benzene or chloroform in small but well-defined prisms, melting at  $160^{\circ}$ – $161^{\circ}$ , and deflagrating at a higher temperature (Zincke).

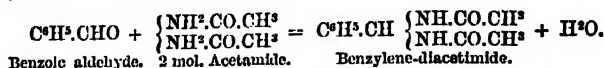
**Diamidobenzyltoluene**  $\text{C}^{11}\text{H}^{12}(\text{NH}_2)_2$ , is formed by treating the dinitro-compound with tin and hydrochloric acid. The product of the reaction is a stannochloride, which crystallises in small very soluble needles. When decomposed by hydrogen sulphide, it yields the *hydrochloride*  $\text{C}^{11}\text{H}^{12}(\text{NH}_2)_2 \cdot 2\text{HCl}$ , which is very soluble in water and alcohol, and can be purified only by recrystallisation from hot dilute hydrochloric acid; it forms white needles or plates. The *sulphate*  $\text{C}^{11}\text{H}^{12}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$  is also very soluble, and crystallises from hot alcohol in long colourless needles. By decomposing the hydrochloride with potash, the free base is obtained as a white crystalline powder. It is freely soluble in alcohol and ether, and the solution darkens when exposed to the air.

**Benzyltoluene-sulphuric acid**.—Benzyltoluene dissolves in hot fuming sulphuric acid, with formation of at least two sulpho-acids; but only the disulpho-acid has been isolated, its potassium salt being almost insoluble in strong alcohol, and crystallising from hot dilute alcohol in white laminae or broad needles, having the composition  $\text{C}^{11}\text{H}^{12}(\text{SO}_3\text{K})_2 + 3\frac{1}{2}\text{H}_2\text{O}$ , and readily soluble in water. The *barium salt*  $\text{C}^{11}\text{H}^{12}(\text{SO}_3)_2\text{Ba} + 8\frac{1}{2}\text{H}_2\text{O}$  separates from an aqueous solution on addition of alcohol in crystalline crusts, which redissolve in water but slowly. The *copper salt*  $\text{C}^{11}\text{H}^{12}(\text{SO}_3)_2\text{Cu} + 4\frac{1}{2}\text{H}_2\text{O}$  crystallises from a hot concentrated solution in small bluish-green laminae, and from dilute alcohol in prisms. The *lead salt* is readily soluble in hot water, sparingly in cold, and forms colourless prisms. The *free acid* is easily soluble in water, alcohol, and ether, and forms a crystalline mass, consisting of long colourless needles melting at  $38^{\circ}$  (Zincke).

**Benzyl-ethyl-benzene**,  $C^{10}H^{14} = C^6H^5-CH^2-C^6H^5-C^2H^5$ , is formed, together with other bodies, by boiling a mixture of benzyl chloride, ethyl-benzene and zinc, as long as hydrochloric acid continues to escape, and separated from the product by fractional distillation. It is a colourless liquid, having a faint aromatic odour, and boiling at  $294^\circ-295^\circ$ . By oxidation it yields benzoic acid, together with a ketone (J. F. Walker, *Deut. Chem. Ges. Ber.* v. 686).

**BENZYLENE-DIACETIMIDE**,  $C^{10}H^{11}N^2O^2 = C^6H^5.CH \begin{Bmatrix} NH.CO.CH^3 \\ NH.CO.CH^3 \end{Bmatrix}$

(E. Roth, *Ann. Ch. Pharm.* clv. 72; *Zeitschr. f. Chem.* [2] iv. 650, vi. 680).—Produced by the action of benzoic aldehyde on acetamide:



To prepare it, about equal parts of acetamide and commercial bitter-almond oil are heated for some hours in a retort having its neck directed upwards. Water, prussic acid, and small quantities of an oil which floats on water, then escape, and the residue in the retort solidifies, on cooling, to a yellowish crystalline mass, which may be freed from bitter-almond oil by treatment with ether, then several times recrystallised from hot water. From the first mother-liquors, ammonia throws down small quantities of a body which appears to be amarine.

Benzylene-diacetamide forms capillary, silky, very bulky crystals, which, when dried in the air, unite into a felted mass. It dissolves sparingly in cold water and in ether, easily in boiling water and in alcohol, melts when heated, and resolidifies in the cold. When its solution is heated with hydrochloric acid, it decomposes with separation of benzaldehyde. Strong potash-solution, on the other hand, does not act upon it, even on prolonged boiling; neither does sodium-amalgam in neutral or a alkaline solution. Benzylene-diacetamide is permanent at  $200^\circ$ , but decomposes at a higher temperature, yielding, as distillation-products, first, acetamide; then, at a considerably higher temperature, oily bodies which do not solidify on cooling, and finally, above the boiling point of mercury, a mixture, recrystallising on cooling; of lophine with an easily soluble base not yet examined.

**BENZYLENE-DIBENZIMIDE**,  $C^{21}H^{18}N^2O^2$ , is prepared by heating bitter-almond oil with benzamide for several hours, treating the product, which solidifies in the crystalline form, with ether, and recrystallising the residue from boiling alcohol. It forms long silky needles, insoluble in boiling water, slightly soluble in ether and cold alcohol, melting at  $197^\circ$ . It dissolves in dilute hydrochloric acid, but the solution, even when only moderately heated, gives up benzoic aldehyde, while benzamide remains dissolved (Roth).

**BENZYLENE-DIBUTYRIMIDE**,  $C^{22}H^{22}N^2O^2$ , was obtained by Strecker from bitter-almond oil and butyramide in the same manner as the acetyl-compound above described. It forms slender crystals, nearly insoluble in cold, sparingly soluble in boiling water, easily soluble in alcohol, moderately soluble in ether. In the preparation of this substance also, small quantities of a light oil are obtained as a secondary product (Roth).

**BENZYL SULPHUROUS ACID**,  $C^7H^7.SO^2H$  (Böhler, *Zeitschr. f. Chem.* [2] iv. 449; Barbaglia, *Deut. Chem. Ges. Ber.* v. 270, 687).—Böhler obtained this acid by boiling benzyl chloride with a moderately strong solution of neutral potassium sulphite:  $C^7H^7.Cl + K^2SO^3 = KCl + C^7H^7.SO^2K$ . The benzyl chloride gradually dissolves, and the concentrated solution on cooling deposits the *potassium salt*  $C^7H^7.SO^2K + H^2O$  in colourless orthorhombic prisms, which give off the whole of their water at  $100^\circ-150^\circ$ . The *barium salt*  $(C^7H^7.SO^2)^2Ba + 2H^2O$  obtained by double decomposition, crystallises in colourless laminae, somewhat sparingly soluble in water. By digesting this salt with dilute sulphuric acid, and saturating the filtrate with lead hydrate, a *basio lead salt*  $(C^7H^7.SO^2)^2Pb.PbH^2O$  is obtained in shining crystals; and, on passing carbonic acid gas into the aqueous solution of this salt, the *neutral lead salt*  $(C^7H^7.SO^2)^2Pb$  separates in anhydrous crystalline laminae. The *ammonium salt*, the *calcium salt*  $(C^7H^7.SO^2)Ca + 2H^2O$ , and the *silver salt*  $C^7H^7.SO^2Ag$ , are crystalline. The *hydrogen salt*, or *free acid*, is obtained by decomposition of the lead or barium salt, in colourless extremely hygroscopic crystals (Böhler).

The *potassium salt*, distilled with cyanide of potassium, yields a volatile cyanide  $C^7H^7.ON$ , which, when boiled with potash, is converted into alpha-toluidine and  $C^6H^5.CH^2CO^2H$ ; this cyanide, is therefore benzyl cyanide  $C^7H^7.CH^2ON$ , and the acid



$C^6H^5SO^2H$ , from the potassium salt of which it is produced as above, is benzyl-sulphurous acid,  $C^6H^5.CH^2.SO^2H$ , and not either of the modifications of toluene-sulphonic acid  $C^6H^5\left\{ \begin{array}{l} CH^2 \\ SO^2H \end{array} \right.$  described in the *First Supplement*, p. 286 (Barbaglia).

When the potassium salt is heated with phosphorus pentachloride, sulphurous oxide is evolved, and the distillate contains benzyl chloride, together with phosphorus oxychloride and a little thionyl chloride  $SOCl^2$ , but no sulphuryl chloride or phosphorus sulphochloride. Hence the group  $SO^2K$  in the potassium salt must be united with the carbon of the group  $CH^2$  through the medium of oxygen, and not through that of sulphur; if the formula of the salt were  $C^6H^5.CH^2-S-O-O-K$ , it would, when distilled with  $PCl^5$ , yield benzyl sulphochloride  $C^6H^5.CH^2-S-O-O-Cl$ . Its constitution formula must therefore be,

either  $C^6H^5.CH^2-O-S-O-O-K$ ,

or  $C^6H^5.CH^2-O-O-S-O-K$ .

With either of these formulae it is easily seen that the replacement of the oxygen-atom next to the benzyl, and of that next to the potassium, by an equivalent quantity of chlorine, will give rise to benzyl chloride and thionyl chloride:

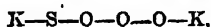
$C^6H^5.CH^2.Cl$   
Benzyl chloride.

$Cl-O-S-Cl$   
Thionyl chloride.

$ClK$ .

The occurrence of sulphurous oxide during the reaction is due to the fact that thionyl chloride easily gives up its two atoms of chlorine in exchange for an atom of oxygen, and will therefore act on the potassium salt,  $C^6H^5SO^2K$ , in a similar manner to the pentachloride of phosphorus. The question as to which of the two formulae above given is the true expression of the constitution of the benzyl sulphite, cannot be determined by the products which it gives with phosphorus pentachloride. That the sulphur-atom is not in immediate union with the potassium, in other words, that the formula of the salt is not  $C^6H^5.CH^2-O-O-S-K$ , may be inferred from the non-occurrence of phosphorus sulpho-chloride,  $PSCl^3$ , as one of the products of the reaction.

The preceding results lead then to the conclusion, that the acid  $C^6H^5SO^2H$ , obtained by the action of benzyl chloride on potassium sulphite, is not a *sulphonic acid*, that is to say, an acid in which the group  $SO^2H$  is united to the carbon through the medium of its sulphur-atom, but an acid sulphurous ether, its proper name being benzyl-sulphurous acid. Further, it appears most probable that the constitution of the sulphites—neutral potassium sulphite, for example—should be represented, not by the formula



but rather by



These conclusions, require however, to be confirmed by the study of other sulphurous ethers prepared by the action of alcoholic chlorides on neutral sulphites (Barbaglia).

When the boiling of the benzyl chloride with potassium sulphite is continued for a long time, a large quantity of sulphurous oxide is evolved, but the layer of oil floating on the saline solution never disappears completely. When distilled with water, and afterwards alone, it yields, besides unaltered benzyl chloride, a considerable quantity of benzyl alcohol and benzoic aldehyde, together with benzyl oxide (Barbaglia). According to Vogt & Henninger (*Ann. Chem. Phys.* [4] xxv. 129) there is also formed a body  $(C^6H^5)^2SO^2$ , isomeric, if not identical, with Otto & Grubert's sulphotoluide (1st *Suppl.* 289): Vogt & Henninger, however, call it *benzyl sulphide*. It is insoluble in water, slightly soluble in alcohol, and crystallises in flattened needles melting at  $150^\circ$ . (Otto & Grubert's sulphotoluide crystallised from alcohol in small tabular prisms melting at  $155^\circ$ – $156^\circ$ ).

Benzyl-sulphurous acid, identical in properties and reactions with that above described, is obtained by the oxidising action of nitric acid on benzyl bisulphide  $(C^6H^5)^2S^2$  (prepared by the action of bromine on an ethereal solution of benzyl sulphhydrate). Benzoic aldehyde is formed at the same time, together with a little benzoic acid; on distilling the product, these bodies pass over with the vapour of water; and on neutralising the residue with sodium carbonate, evaporating, treating the residue with alcohol, and leaving the solution to evaporate, potassium benzyl sulphite is deposited in yellowish laminae, which may be rendered colourless by repeated crystallisation, or by treatment with tin and hydrochloric acid, or with sodium-amalgam, whereby adhering nitro-compounds are destroyed.

**Benzylsulphurous Chloride**,  $C^6H^5.CH^2.SO^2Cl$ , formed by the action of phosphorus pentachloride on potassium benzylsulphite, crystallises in prisms melting at  $92^\circ$ , and decomposing at a higher temperature into sulphur dioxide and benzyl chloride. Concentrated ammonia converts it into the amide,  $C^6H^5.CH^2.SO^2NH^2$ , which crystallises from water in small prisms melting at  $105^\circ$  (Limpricht, *Deut. Chem. Ges. Ber.* vi. 534).

**Chlorobenzylsulphurous acid**,  $C^6H^4Cl.CH^2.SO^2H$ , is obtained as a potassium salt by boiling chlorobenzyl chloride  $C^6H^4Cl.CH^2Cl$  (obtained by the action of chlorine on chlorotoluene) with potassium sulphite. The solution on cooling deposits the potassium salt,  $C^6H^4Cl.CH^2.SO^2K$ , in colourless needles, which, according to Böhler (*loc. cit.*) are anhydrous, but according to Vogt & Henninger (*Ann. Ch. Phys.* [4] xxv. 129) contain a molecule of water, which they give off at  $180^\circ$ ; they are soluble in water and in boiling alcohol. The **barium salt**  $(C^6H^4Cl.CH^2.SO^2)^2Ba + H^2O$ , obtained by double decomposition, forms colourless shining crystals. The **basic lead salt**  $(C^6H^4Cl.CH^2.SO^2)^2Pb.PbH^2O^2$ , prepared by decomposing the barium salt with sulphuric acid, and neutralising with lead hydrate, forms silvery crystalline scales (Böhler). According to Vogt & Henninger, these chlorobenzylsulphites, though they appear to be homogeneous, nevertheless consist of mixtures of two isomerides, for when fused with potash they yield both salicylic and paraoxybenzoic acid.

The action of potassium sulphite on chlorobenzyl chloride likewise gives rise to chlorosulphotoluide  $(C^6H^4Cl)^2SO^2$  (called *chlorobenzyl sulphide* by Vogt & Henninger). This compound is insoluble in water, and after washing with water and with ether, and crystallisation from boiling alcohol, is obtained in colourless needles. The mother-liquor of these crystals contains two other bodies, melting at  $149^\circ$  and  $185^\circ$  respectively (Vogt & Henninger).

**Benzylene Chloride**  $C^6H^5.CHCl^2$ , metameric with chlorobenzyl chloride, yields, when boiled with potassium sulphite, only a small quantity of a sulpho-acid not yet examined, the chief product of the reaction being benzoic aldehyde (Böhler).

**Nitrobenzylsulphurous acid**,  $C^6H^4(NO^2).CH^2.SO^2H$ . The **barium salt** of this acid, obtained by dissolving barium benzylsulphite in fuming nitric acid, crystallises in shining colourless needles containing  $[C^6H^4(NO^2).CH^2.SO^2]^2Ba + 2H^2O$ . By decomposing it with sulphuric acid and neutralising the filtered solution with lead hydrate, a **basic lead salt**  $[C^6H^4(NO^2).CH^2.SO^2]^2Pb.PbH^2O^2$  is obtained in colourless needles. The **neutral lead salt**  $[C^6H^4(NO^2).CH^2.SO^2]^2Pb + H^2O$  forms beautiful needle-shaped crystals more soluble than the basic salt (Böhler).

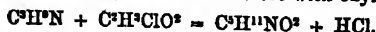
**BERAUNITE**. This mineral, hitherto known only as a pseudomorph after vivianite, from the Hrbek iron mine, at St. Benigna in Bohemia, (i. 579), has lately been found implanted on brown hematite, in the Father Abraham mine at Scheibenberg in Saxony. It forms laminar and radiate groups, also separate laminae and rods running out in crystalline points, which indicate the form of gypsum. Colour, hyacinth-red to reddish-brown; lustre, nacreous to silky; streak-powder, yellow. Sp. gr. 2.983. Analysis gave 54.50  $Fe^2O^3$ , 28.65  $P^2O^5$ , and 16.55 water, agreeing nearly with the formula  $5Fe^2O^3.3P^2O^5 + 14H^2O$  (Fronzel, *Jahrbuch f. Mineralogie*, 1873, 23).

**BERYL**. A specimen of this mineral from Elba, of sp. gr. 2.699–2.710, was found to contain:

$SiO^2$	$Al^2O^3$	$Fe^2O^3$	$GIO$	$Ca^2O$
70.00	26.33	0.40	3.31	0.88 = 100.92.

It differs from all the beryls hitherto analysed in containing a smaller percentage of glucina and a larger proportion of alumina, and by the presence of caesia (E. Bechi, *Jahrbuch f. Mineralogie*, 1872, 95).

**BETAINE**,  $C^3H^{11}NO^2$ . (Schoibler, *Zeitschr. f. Chem.* vi. 505; Liebreich, *ibid.* 508).—This base, obtained from beet-juice (1st Suppl. 340), is identical with that which is produced by the action of trimethylamine on monochloroacetic acid, that is to say, trimethyl-glycoccine  $C^3H^2(CH^3)^3NO^2$  and therefore with oxyneurine:



When fused with potassium hydrate, it gives off a large quantity of pure trimethylamine.

Betaine is not poisonous. The crystals of the hydrochloride, according to measurements by P. Groth, are monoclinic; they are thick, tabular, 10 mm. long and broad, and cleave with moderate distinctness parallel to the clinopinacoid, ( $\infty P\infty$ ). The tribasic phosphate and the oxalate have been obtained in fine crystals; the malate and tartrate only in syrupy or hygroscopic masses (Schoibler).

For preparing betaine from the juice or molasses of beet, Scheibler now recommends that the liquid be first mixed with a slight excess of basic lead acetate, to precipitate various acids and colouring matters, which would interfere with the purification of the betaine to be subsequently separated. The filtrate from the lead precipitate is mixed with excess of dilute sulphuric acid to remove the lead; and from the acid filtrate the betaine is obtained by means of sodium phosphotungstate in the manner formerly described.

Liebreich boils the diluted molasses for twelve hours with barium hydrate; filters after removing the excess of baryta with carbonic acid; evaporates; exhausts the remaining treacly mass with alcohol; mixes the concentrated alcoholic extract with an alcoholic solution of zinc chloride; purifies the resulting precipitate by recrystallisation from water; and precipitates its aqueous solution with baryta-water. The liquid filtered from the precipitated zinc oxide contains a corresponding quantity of barium chloride. The barium is precipitated with the exact quantity of dilute sulphuric acid required; and on evaporating the filtrate, the hydrochloride of betaine crystallises out.

The juice of the beet in the earlier stages of growth contains a larger proportion of betaine than that of older beet, the proportion, of the base decreasing as that of the sugar increases with the ripening of the plant. Young beets gathered on July 1 yielded a juice containing about  $\frac{1}{4}$  p.c. betaine, whereas ripe beets from the same field taken up on October 1, yielded only  $\frac{1}{10}$  p. c., of betaine (Scheibler).

**Betaine of the Phosphorus series or Trimethyl-phosphorylglycine,**  $C_3H_7PO_2 = C_3H_7(CH_3)_3PO_2$ . (A. II. Meyer, *Deut. Chem. Ges. Ber.* iv. 734; *Chem. Soc. J.* [2] ix. 1066). The hydrochloride of this base,  $C_3H_7PO_2.HCl$ , is produced by heating 1 mol. trimethylphosphine with 1 mol. chloroacetic acid to  $100^\circ$  in a sealed tube for five or six hours. It unites with platinum chloride, forming a platinumchloride  $2(C_3H_7PO_2.HCl).PtCl_4$ , and when treated with sulphuric acid, yields a sulphate from which the free base may be precipitated by baryta-water. The base is a very hygroscopic crystalline mass, neutral to vegetable colours, and forming crystalline salts with hydriodic and with nitric acid.

The homologous compound, *triethyl-phosphorylglycine*,  $C^6H^{17}PO_2 = C^6H^{17}(C^2H^5)_3PO_2$ , is obtained in like manner by the action of chloroacetic acid on triethylphosphine (Hofmann, *Proc. Roy. Soc.* xi. 525).

**Aromatic Betaines,** (Griess, *Deut. Chem. Ges. Ber.* vi. 585).—These bases, analogous in constitution to the betaine of the fatty series (trimethyl-glycine), are produced by the action of methyl iodide in presence of methyl alcohol and an alkali on amidated aromatic acids, three atoms of hydrogen being replaced by methyl.

*Benzbetaine\**,  $C^6H^{13}NO_2$ , which has the composition of trimethyl-amidobenzoic acid,  $C^6H^9(CH_3)_3NO_2$ , is prepared by pouring methyl alcohol on amidobenzoic acid, adding three times as much strong potash-ley as is necessary to neutralise the acid, and then methyl iodide in the proportion of 3 mol. to 1 mol. of the amidobenzoic acid. The mixture is left to itself for three days, the methyl alcohol then distilled off, hydriodic acid added in excess, and the hydriodide of benzbetaine, which crystallises out, is decomposed by lead hydrate, which separates the base.

Benzbetaine crystallises in small white needles containing 1 mol. water of crystallisation, which is easily given off at  $105^\circ$ . It is insoluble in ether, very soluble even in cold alcohol, and deliquesces on exposure to the air. It is neutral to vegetable colours, and has a strong bitter taste.

The *hydriodide*,  $C^6H^{13}NO_2.HI + H^2O$ , crystallises in small short prisms, which dissolve very sparingly in cold, easily in hot water or alcohol, but are quite insoluble in ether. The *platinchloride*,  $2(C^6H^{13}NO_2.HCl).PtCl_4 + 4H^2O$ , crystallises in prisms sometimes of considerable size, slightly soluble in hot, very slightly in cold water.

When anhydrous benzbetaine is heated to its melting point, it is converted into the isomeric methylic ether of dimethyl-amidobenzoic acid,  $C^6H^{11}\{N(CH_3)_2\}COOCH_3$ , a yellowish liquid having an aromatic odour, boiling at  $270^\circ$  (uncorrected), heavier than water and insoluble therein, but dissolved by cold dilute acids, with formation of saline compounds. Its *sulphate*,  $C^6H^{11}\{N(CH_3)_2\}COOH.H_2SO_4$ , crystallises in very small prisms, easily soluble in cold water, sparingly soluble in dilute sulphuric acid.

\* In Griess's memoir, this compound is called trimethyl-benzbetaine, and the corresponding anisic compound trimethyl-anisbetaine; but the prefix 'trimethyl' is surely superfluous: the base  $C^6H^9(CH_3)_3NO_2$  is called betaine, not trimethyl-betaine, and by analogy, the base  $C^6H^{13}(CH_3)_3NO_2$  should be called benzbetaine.

The *platinochloride*,  $2 \left[ C^H \cdot \left\{ \begin{smallmatrix} N(CH^3)_2 \\ COOCH^3 \end{smallmatrix} \right\} \cdot HCl \right] \cdot PtCl^4$ , forms spindle-shaped laminae, very slightly soluble in cold water.

*Anis betaine*  $C^H H^3 NO^2 = C^H \cdot N(CH^3)_2 O^2$ , which has the composition of trimethyl-amidanisic acid, is produced in like manner by the action of methyl iodide on amidanistic acid. It crystallises from aqueous solution in large, generally very well-defined prisms, sometimes an inch long, having a vitreous lustre, and containing 5 mols. water of crystallisation. It is very easily soluble in hot, moderately soluble in cold water, less soluble in alcohol, and quite insoluble in ether. Like benzbetaine, it has a bitter taste and is neutral to vegetable colours. The *hydriodide*,  $C^H H^3 NO^2 HI + H^2 O$ , forms white shining needles, sometimes an inch long, moderately soluble in hot, very slightly in cold water, apparently less soluble in alcohol, and quite insoluble in ether.

The *platinochloride*,  $2(C^H H^3 NO^2 \cdot HCl) \cdot PtCl^4$ , crystallises in narrow yellow laminae, very slightly soluble in cold water.

By dry distillation, anisbetaine is transformed, like the preceding compound, into the methylic ether of dimethylamidanic acid,  $C^H H^3 \left\{ \begin{smallmatrix} N(CH^3)_2 \\ OCH^3 \\ COOCH^3 \end{smallmatrix} \right.$ , which is a yellowish liquid, having a faint aromatic odour, insoluble in water, and boiling at  $288^\circ$  (uncorrected.)

**SEYRICHITE.** A native sulphide of nickel from the Westerwald. See NICKEL.

**BILE.** *Modification of Pettenkofer's test.* G. Strassburg, (*Pflüger's Archiv. f. Physiologie*, iv. 461), in testing icteric urine for bile-acids by Neukomm's improved form of Pettenkofer's test (1st Suppl. 341), obtained only a yellow, but never a cherry or violet colour, showing that the quantity of these acids in the urine, even in cases of intense jaundice, is very small. The following method was, however, found to give certain indications: A piece of filtering paper is dipped into the urine previously mixed with a little cane-sugar, and allowed to dry; a drop of pure sulphuric acid is then put upon it, and allowed partially to run off. In a quarter of a minute, a beautiful violet colour appears, best seen by transmitted light. By this means, 0.00003 gram of glycocholic acid can be detected. The great delicacy of the test is, perhaps, due to the absence of water, whereby the charring, which would otherwise occur and obscure the reaction, is prevented.

The spectrum yielded by the violet-red liquid obtained in treating sodium glycocholate with sugar and sulphuric acid for Pettenkofer's test, consists of three bands, one extending from midway between C and D to D, the second midway between D and E, and the third between  $\delta$  and F (Heynsius u. Campbell, *Pflüger's Archiv. f. Physiologie*, iv. 497).

*Action of Bile on Starch.*—According to v. Wittich (*Pflüger's Archiv. f. Physiologie*, vi. 181), fresh human bile possesses the power of converting starch into sugar, a property previously observed by Masse in the bile of the pig. Boiled starch mixed with 20 to 30 drops of human bile, and left for an hour at the ordinary temperature, exhibited a distinct sugar reaction with copper sulphate. The bile mixed with absolute alcohol as long as it exhibited turbidity, left, on filtration, a residue which, on being treated with glycerin, yielded an extract, exhibiting after 24 hours an energetic diastatic action. Still more active was the alcoholic precipitate of the extract dissolved in water.

**BILE-PIGMENTS.**—Bilirubin and other bile-pigments, treated with oxidising agents, yield a blue product, called bilicyanin, produced by moderate oxidation, and a brown substance called cholestin, resulting from more complete oxidation. These products have been studied by Maly (*Wien. Akad. Ber. [zweite Abth.]* lix. 597; *Jahresb.* 1869, 817) and by Heynsius u. Campbell (*Pflüger's Archiv. f. Physiologie*, iv. 497). Bilicyanin is best obtained by adding an alcoholic solution of bromine to bilirubin suspended in chloroform. If the liquid be left to evaporate as soon as it exhibits a pure blue colour, there remains a shining dark mass, which appears dark green when spread in a thin layer upon porcelain, but dissolves with splendid blue colour in alcohol; it is less soluble in ether, more freely in ether-alcohol. The blue alcoholic solution (containing a little hydrobromic acid), exhibits the following reactions: on gently heating it with weak nitric acid, the blue colour passes slowly through violet and purple-red to light brown; with caustic potash a dingy sap-green liquid is produced, becoming blue again on addition of hydrochloric acid; with ammonia, a dark indigo-blue liquid, which becomes bright blue on addition of hydrochloric acid.

solution of neutral lead acetate forms a dark green-blue precipitate; silver nitrate merely throws down a little silver bromide, and on adding ammonia to the filtrate, a black-brown precipitate is formed, which dissolves in a mixture of alcohol and acetic acid, with a violet colour, changing to fine blue. With hydrochloric acid and zinc, the blue solution slowly becomes dark green, then sap-green; hydrochloric acid alone does not alter the colour. Hydrogen sulphide forms a bright green solution, and then flocks of biliverdin, the liquid becoming nearly colourless. On mixing the liquid with a few drops of nitric acid, and pouring it upon sulphuric acid, so as to form a supernatant layer, the remainder of the bile-pigment is obtained with very fine colour. Ammonia and calcium chloride slowly form a precipitate of dark indigo-blue colour (Maly).

According to Heynsius and Campbell, bilicyanin prepared as above, is not a perfectly definite product, as it exhibits various degrees of solubility, and gives two, or perhaps three absorption-spectra in the yellow and green. It does not exist in natural bile-pigment till after oxidation by exposure to the air or otherwise. It exists in gall-stones and probably in urine, inasmuch as it reacts with hydrochloric acid somewhat like indican, and may have been mistaken for that substance in urine.

Choletelin, the end-product of the oxidation, is best obtained by passing nitrous vapours into alcohol in which bilirubin or bilihumin is suspended. If the alcoholic solution be then poured into water, nearly the whole of the colouring matter separates in flakes of the colour of ferric oxide, which in many cases soon become denser, and are easy to filter and wash; they dry up to a brown powder. Choletelin cannot be made to crystallise from any solvent. It dissolves very easily in the fixed alkalis and their carbonates, also in ammonia, forming brown solutions, from which it is precipitated in flocks by acids. It is soluble in alcohol, ether, and chloroform. The alcoholic solution is precipitated by water; with silver nitrate it gives a precipitate only on addition of ammonia. No perceptible reaction is produced by hydrogen sulphide, or by zinc and hydrochloric acid.

The quantity of bromine used in the formation of choletelin shows that it is formed from bilirubin by assumption of 3 atoms of oxygen. Its analysis gave numbers leading to the formula  $C^{18}H^{18}N^2O^3$  (= bilirubin — C + 3O); but as neither carbonic nor formic acid appears to be produced at the same time, Maly is of opinion that its true formula is  $C^{18}H^{18}N^2O^4$ . Silver nitrate added to a solution of choletelin in a small quantity of dilute aqueous ammonia throws down red-brown flocks, which separate from a nearly colourless liquid: the second of three fractional precipitations yielded an amount of silver agreeing with that of the bibasic compound  $C^{18}H^{18}Ag^2N^2O^4$ . Choletelin is not much attacked by strong nitric acid, and in particular does not yield any picric acid. By dry distillation with soda-lime it yields a tarry distillate not containing either aniline or phenol (Maly).

Choletelin does not give Gmelin's pigment reaction (the change of colour from green to blue, violet, red, and yellow produced by treating bile-pigments with nitric acid containing nitrous acid). Its spectrum is more constant than that of bilicyanin, consisting of one broad absorption-band extending from *b* to a little beyond *F*, when in acid solution; in an alkaline solution the band is somewhat less refrangible. Choletelin may be detected by its spectroscopic characters in icteric urine, but is never found in normal urine or in gall-stones (Heynsius & Campbell).

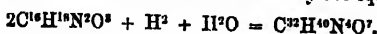
*Reducible Product of the Oxidation of Bile-pigments* (Stokvis, *N. Rep. Pharm.* xxi. 123).—This substance is formed as a secondary product in most cases of the oxidation of biliary colouring matter whereby Gmelin's reaction is produced. It is colourless, or of a light yellow tint, and is soluble in water, alcohol, and dilute acids. It becomes of a beautiful rose-red colour when boiled with reducing agents in alkaline solutions. The red solution gives in the spectrum a tolerably broad absorption-band in the green. In concentrated solutions (thick strata) the band begins close on the line *D*, and extends to *b*. In dilute solutions (thin strata) it occupies only two-thirds of the space between *D* and *E*, ending short of *E*. Shaking with air causes both the rose colour and the absorption-band to disappear. This by-product differs from the bile colouring matter and other oxidation-products of the same, in being insoluble in chloroform and ether, and in not forming insoluble compounds with neutral or basic lead acetate. It is precipitated however by ammonia and basic lead acetate.

This substance exists as such in the gall-stones both of man and of the ox. It can be obtained from them by simple boiling with distilled water, and extraction with dilute acids. It does not exist in fresh bile. It occurs in the urine of animals which have been starved for some days previously, in icteric urine, and in the urine of febrile diseases, such as small-pox, typhus, &c. It is not found in healthy urine. It seems to be present in the alimentary canal, although in direct experiments with different kinds of food little or none could be found. In alkaline solutions it soon loses its

characteristic properties. Its occurrence in any liquid of neutral or acid reaction affords an indication of the previous existence of bile-pigments therein. In applying the test, the liquid is to be precipitated with lead acetate, excess of lead removed by oxalic acid, and the filtrate concentrated and boiled with alkalis and a reducing agent. If no reduction takes place, and if the other tests for biliary colouring matter have given a negative result, their absence may be safely inferred.

**Blue Colouring matter of Bile.** E. Ritter (*N. Rep. Pharm.* xx. 569) describes a blue colouring matter, which appears to be a constituent of the bile itself, and not a product of oxidation, like the blue pigment above described, or those which Städeler and Jaffé have obtained by the action of nitric acid on the natural pigments of the bile. Ritter finds this substance in the bile of man, and in that of the ox, sheep, pig, dog, and cat. To prepare it, bile is shaken with chloroform, till a yellow solution is obtained, and the yellow chloroform solution is treated with sodium carbonate till the colour entirely disappears. On neutralisation with hydrochloric acid, two layers are formed, one of which contains the yellow chloroform solution, the other the blue colouring matter in a state of suspension. This colouring matter is insoluble in chloroform and acids. It dissolves in alkalis, forming a colourless or yellowish solution. When this solution is neutralised with acids and exposed to the air, a brown precipitate is formed, which becomes blue again, sometimes in a few days, sometimes only after a month. In this respect it differs from reduced indigo, which, when dissolved in alkalis, instantly turns blue on exposure to the air.

**Conversion of Bilirubin into Urinary Colouring matter:** Hydrobilirubin. When bilirubin is dissolved in dilute soda or potash-ley, and sodium-amalgam is added, air being excluded, no hydrogen is evolved, but the dark colour gradually lightens; after two or three days' action, the solution acquires a yellow or bright brown-yellow colour, and then gives off hydrogen. From this liquid hydrochloric acid separates a pigment, which seems to be a weak acid, yielding with alkalis brown-yellow soluble salts, and with heavy metals insoluble compounds which separate in red flakes; it is readily soluble in alcohol, slightly in water, readily in ammonia and fixed alkalis, also in ether, liquid hydrocarbons, glacial acetic acid, and chloroform. Its spectrum has a characteristic dark black absorption-band between the green and blue (Fraunhofer's lines *D* to *F*) more marked in acid solution than in alkaline. This product appears to be identical with the urobilin of Jaffé (*Virchow's Archiv.* xlvii), obtained from normal and febrile urine; it also agrees with the product from excrement obtained by Vaulair and Masius (*Centralbl. f. d. Med. Wissensch.* 1871, No. 24), and with the urinary colouring matter obtained by Scherer. It contains about 1.5 p. c. carbon less, and about as much per cent. hydrogen more than bilirubin, and may therefore be appropriately called hydrobilirubin. Its composition may be represented by the formula  $C^{22}H^{16}N^2O^7$ , and its formation from bilirubin by the equation:



Its formation in the intestine from the colouring matter of the bile is essentially the same process as that with sodium-amalgam, inasmuch as abundance of hydrogen is generated in the intestine and immediately exerts a hydrogenising action.

Biliverdin appears to be acted upon by sodium-amalgam in the same manner as bilirubin (*R. Maly, Ann. Ch. Pharm.* clxi. 368; clxiii. 77).

**BISMUTH.** A specimen of native bismuth from Peru, analysed by G. Barth, (*Vierteljahrsschrift pr. Pharm.* xviii. 580), was found to contain 98.372 p. c. bismuth, 4.670 antimony (with a little tin), and 2.058 copper (with a little iron), no sulphur or arsenic.

**Fusion and Volatilisation.**—According to A. von Riemadyk (*Chem. News*, xx. 32), bismuth melts at 268.3°, and does not volatilise sensibly at temperatures considerably above its melting point. At a bright red heat, 2.3433 grams of bismuth lost in an hour 1 milligram in weight.

**Detection of Bismuth in presence of Lead and Antimony.**—Small quantities of bismuth in presence of lead or antimony, may be detected by the characteristic red coating which, as observed by v. Kobell, (p. 102), is produced when bismuth is heated on charcoal with a mixture of potassium iodide and sulphur. The same reaction may be obtained by heating the substance under examination with an equal weight of a mixture of 5 parts sulphur and 1 part potassium iodide in an open tube 4 inches long and not less than half an inch wide.

When pure lead oxide is thus treated, part of the sulphur sublimes and condenses above the assay, its heavy vapours also burning at the lower end of the tube. The

copious yellow fumes pass through the tube, and an abundant sublimate condenses, beginning about one-third of an inch above the assay, and becoming bright yellow when cold.

*Lead oxide, with 1 p. c. of Bismuth trioxide*, exhibits the same phenomena as above, but one-third of an inch above its lower edge the yellow sublimate is replaced by a broad and distinctly red ring of the bismuth sublimate.

*Lead oxide, with  $\frac{1}{2}$  p. c. of Bismuth trioxide*, gives the same reaction as in the last experiment, but the bismuth sublimate is orange-red, but still so distinctly marked as to leave no doubt that even a smaller proportion of bismuth could be detected.

*With 50 parts of Lead oxide, 50 parts of Antimony trioxide, and 1 part of Bismuth trioxide*, the white antimonial sulphide entirely conceals the bismuth reaction. To obviate this, the mixture of the three oxides is mixed with an equal volume of sulphur, and treated with the blue flame for several minutes; and the resulting fused sulphides are removed to a flat coal, and treated alternately with the oxidising and reducing flames, until the antimonial fumes have nearly ceased, and an impure blue lead flame appears. The residue, powdered and treated as before in the open tube, yields a distinct bismuth sublimate, about one-third of an inch above the lower edge of the yellow sublimate.

Care must be taken not to confound with the bismuth sublimate, a sublimate of iodine, which may condense in the upper part of the tube, but at a greater distance from the assay (H. B. Cornwall, *Chem. News*, xxvi. 150).

*Assay of Cupreous Bismuth ores*.—The direct separation of bismuth from ores containing a large proportion of copper is attended with considerable difficulty, inasmuch as copper and bismuth behave in the same manner with nearly all metallurgic reagents. In presence of an alkaline flux, however, bismuth sulphide is instantly reduced by carbonaceous matter, while copper sulphide is unattacked. The application of this reaction is as follows:

If the metals exist already in the state of sulphides, it is only necessary to fuse them with the ordinary reducing mixture, to which a little sulphur has been added, to prevent any desulphuration of the copper by the alkali. The yield of bismuth is tolerably free from copper. In the treatment of oxidised ores, the operation is conducted in a similar manner, but a larger amount of sulphur is required, since the whole of the metals have to be sulphurised. The following proportions are recommended for the flux:—Sodium carbonate, 5 parts; salt, 2 parts; sulphur, 2 parts; charcoal, 1 part. Two or three parts of this flux are required for the reduction of three parts of ore.

In the extraction of bismuth by the sulphur-carbon process, there is a loss of about 8 p.c. of the bismuth contained in the ore. Although this loss is unavoidable, it is partly compensated by the elimination during the operation of a considerable quantity of arsenic, antimony, and lead, so that the crude metal obtained by this process is not so impure as the corresponding metal obtained by the direct reduction of the oxidised ore (Hugo Tamm, *Chem. News*, xxv. 85).

*Refining of Crude Bismuth*.—To separate arsenic, the bismuth is melted at a bright red heat, under a cover of borax, and strips of iron are plunged into the molten metal. The arsenic rapidly combines with the iron, forming an arsenide, which rises to the surface of the metal. When the iron is no longer attacked, the whole is allowed to cool, and the bismuth, while still fluid, decanted from the iron arsenide, which solidifies more rapidly.

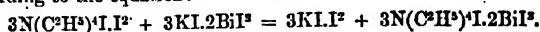
Antimony is most easily separated by melting the alloy with a quantity of bismuth oxide equal to three times the weight of antimony contained in the metal. The bismuth oxide is instantly reduced to the metallic state, while the antimony is converted into oxide. The latter, in combination with a little bismuth oxide, floats on the surface of the pure metal, whence it can be easily removed.

Copper may be completely separated from bismuth by treating the alloy, at a low red heat, with potassium sulphocyanate. One part of a mixture of 8 parts of potassium cyanide and 3 parts of sulphur is thrown over 16 parts of the metal melted at a low temperature. As soon as the reaction takes place, the crucible is covered, and when all deflagration has ceased, the metal is well stirred with a clay stirrer, the flux allowed to set, and the fluid metal poured out. The bismuth will be found perfectly free from copper (Tamm, *ibid.* 100).

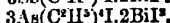
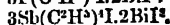
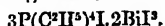
*Electrolysis of Bismuth oxide*.—The fused oxide is easily reduced by the current of 12 Bunsen's elements. If copper poles are used, the negative pole soon becomes covered with metallic bismuth; with platinum wires, an alloy of bismuth and platinum is formed, which melts and drops off. In the solid state the oxide does not conduct (P. Buckhard, *Zeitschr. f. Chem.* vi. 212).

**Bismuth-salts of Organic Bases.** Jörgensen (*J. pr. Chem.* [2] iii. 328) has prepared a series of well-crystallised double salts containing bismuth, and represented by the general formula  $3R(C^2H^3)^4R'.2BiR^2$ , in which  $R=N, P, As$  or  $Sb$ ;  $R'=I, Br, Cl$ . The iodine-compounds are red, or brownish-red, the bromine-compounds yellow, or occasionally brownish-yellow, the chlorine-compounds colourless.

The iodine-derivatives are produced by precipitating a hot alcoholic solution of the periodide of an organic base with potassium-bismuth iodide or with hydrogen-bismuth iodide. Thus the tetrethylammonium-bismuth iodide,  $3N(C^2H^3)^4I.2BiI^2$ , is formed according to the equation:



The ethylphosphonium, ethylstibonium, and ethylarsonium compounds have a composition similar to that of the nitrogen salt, viz.:



The bromine and chlorine derivatives are prepared by precipitating the hot alcoholic solution of the periodide with a solution of bismuth hydrate in strong hydrobromic or hydrochloric acid respectively. The tetrethylammonium-bismuth bromide has the composition,  $3N(C^2H^3)^4Br.2BiBr^2$ ; the chloride,  $3N(C^2H^3)^4Cl.2BiCl^2$ . Corresponding phosphorus, arsenic, and antimony compounds have also been obtained.

**BISMUTHITE.** This mineral, consisting of hydrated bismuth carbonate, occurs, together with Joscite, at San João (José) di Madureira in Brazil, in small stratified lumps, which appear to inclose a number of pseudomorphous prismatic crystals; the recently fractured surface exhibits, under the lens, the appearance of pyromorphite. The mineral is very soft, and has a specific gravity of 5.66. The powder is grass-green, and retains its colour when boiled with potash, but is immediately blackened by ammonium sulphide. Heated in a tube before the blowpipe, the mineral decrepitates, gives off a large quantity of water, and becomes brownish. On charcoal it melts very easily, and is reduced with intumescence. It dissolves in nitric acid, especially when heated, with evolution of carbonic anhydride. Fused on charcoal with sulphur, and then with potassium iodide, it yields a bright red deposit of bismuth iodide (v. Kobell, *Jahrbuch f. Mineralogie*, 1871, 939).

**BISMUTHOFERRITE.** A silicate of iron and bismuth from Schneeberg in Saxony, occurring both in crystals and in finely granular, compact, and earthy forms. Two specimens analysed by Frenzel were found to contain:

$SiO^2$	$Fe^2O^2$	$Bi^2O^2$
23.08	33.33	43.26 = 99.67
24.05	33.12	42.83 = 100

agreeing nearly with the formula  $Bi^2O^2.2Fe^2O^2.4SiO^2$ , or perhaps  $Bi^2O^2.SiO^2 + 2Fe^2O^2.3SiO^2$ , which requires 23.44  $SiO^2$ , 31.25  $Fe^2O^2$ , and 45.31  $Bi^2O^2$  (Frenzel, *Jahrbuch f. Mineralogie*, 1872, 1321; 1873, 478).

The massive green iron ore containing bismuth, found also at Schneeberg, and known as *hypochlorite*, is probably a mixture of bismuthoferrite with quartz and another body of yet undetermined constitution. See *HYPOCHLORITE*.

**BITTER ALMOND OIL.** This liquid is often adulterated with nitrobenzene. The adulteration cannot be detected with certainty by the density, for though nitrobenzene is much heavier than pure bitter-almond oil, it is possible that alcohol may also have been added, which will diminish the density. Neither can the formation of aniline from nitrobenzene by the action of nascent hydrogen be relied upon, since this reaction does not take place in presence of a large quantity of bitter-almond oil. A very delicate test of purity is, however, obtained by agitating the suspected oil with half its weight of caustic potash. If nitrobenzene is absent, only a yellowish colour is thereby produced, but in presence of nitrobenzene the yellow becomes first yellowish-red, then green; and on adding water, the mixture separates into two layers, the lower yellow and the upper green (Bourgoin, *Bull. Soc. Chim.* xvii. 243).

The quantity of nitrobenzene present may be approximately determined by shaking 5 to 10 grams of the essence in a wide-mouthed bottle with 20 to 40 c.c. of concentrated solution of acid sodium sulphite, which precipitates the benzoic aldehyde, then adding ether, filtering quickly, evaporating off the ether, and weighing the residue of nitrobenzene. The quantity of nitrobenzene thus formed is about 90 p.c. of the total quantity present in the bitter-almond oil (Bourgoin, *ibid.* xviii. 113).

**BIURET.**  $C^2H^4N^2O^2$ . This body, which Wiedemann obtained by the action of heat upon urea (*Ann.* 1800) has lately been further studied by Hofmann (*Ann. Chem.*



*Gas. Ber.* iv. 262). The transformation of urea into biuret takes place so easily that the reaction may be used as a test for urea, or as a lecture experiment. It is only necessary to heat half a gram or even less of urea until ammonia escapes, to obtain a considerable quantity of biuret, the presence of which is shown by dissolving the residue in water, and adding a few drops of a solution of copper sulphate and an excess of soda. If very little copper sulphate has been taken, the liquid assumes a pale red colour, but if an excess has been used, a deep violet colour appears.

To prepare large quantities of biuret, urea is heated, according to Wiedemann's direction, in an oil-bath to 150°-160° till the residue no longer dissolves completely in water. The product is now boiled out with water, and the biuret, which separates out on cooling, is obtained in a perfectly pure state by recrystallising it repeatedly from water and at last from dilute ammonia. From the insoluble residue a large quantity of cyanuric acid may be obtained; the mother-liquors of the biuret contain undecomposed urea, which may be employed in a second operation.

Biuret is not readily soluble in cold water, as Wiedemann states; 100 parts require at 0°, 8025 parts; at 15°, 6493 parts; and at 106° (the boiling point of the concentrated solution), 222 parts of water. Wiedemann obtained it only in granular crystals; but if biuret is completely freed from cyanuric acid by crystallising it from alcohol, it crystallises in fine long needles, and is identical and not isomeric with the body, called *isobiuret*, which Baeyer obtained by the action of ammonia upon tribromacetyl-urea (1st Suppl. 349).

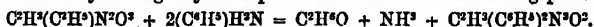
Biuret is also formed by heating ethylic allophanate with aqueous ammonia in sealed tubes to 100°:



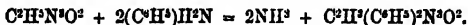
The melting point of biuret is stated differently by different authors; the reason of this is, that the melting point is also the temperature of decomposition, and varies according to the quantities taken or the mode of heating.

Ethylamino does not act upon ethylic allophanate; if the two substances are heated together in sealed tubes to 160°, the same decomposition takes place that would be produced by water alone, the products being urethane, carbon dioxide, and ammonia.

*Diphenyl-biuret*,  $C^6H^5N^2O^2 = C^6H^5(C^6H^5)^2N^2O^2$ .—This compound has been obtained in two modifications, distinguished as  $\alpha$  and  $\beta$ . The former, which is slightly soluble in alcohol and crystallises therefrom in densely interwoven needles melting at 210°, is formed by heating ethylic allophanate with aniline to the boiling point:



The same body is formed directly when aniline is boiled for some time with biuret:



$\beta$ -Diphenyl-biuret is formed by pouring an alcoholic solution of ammonia on finely powdered phenylic isodicyanate:



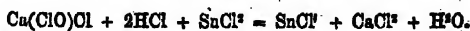
It is insoluble in water, slightly soluble in ether, more easily in alcohol. The boiling saturated alcoholic solution deposits well-formed prisms with truncated pyramidal summits, melting at 165°.

*Triphenyl-biuret*,  $C^6H^5N^2O^2 = C^6H^5(C^6H^5)^2N^2O^2$  is formed by prolonged digestion of 1 mol. phenyl isodicyanate with 1 mol. aniline. The two bodies unite into a crystalline mass, from which, by recrystallisation from alcohol, prisms with terminal planes are obtained. This body closely resembles urea, but melts at 147°, instead of 285° (*Hofmann, Deut. Chem. Ges. Ber.* iv. 250).

**BLACK CUMKIN.** See NIGELLA.

**BLACK SNAKE-ROOT.** See CIMICIFUGA.

**BLEACHING POWDER.** A new method for estimating the available chlorine in bleaching powder is given by J. Horreschoff (*Chem. News*, xxiii. 293). It is based upon the fact that when bleaching powder is made to act upon an excess of stannous chloride in strongly acid solution, stannic chloride is formed at the expense of the available chlorine in the former. The reaction is represented by the following equation:—



The excess of stannous chloride is afterwards estimated by means of a standard solution of potassium dichromate, and deducted from the amount originally employed:



2nd Sup.

The process is conducted in the following manner:—  
 12·8738 grams of pure potassium dichromate are dissolved in water, and the solution diluted to 1 litre. 1·0 c.c. of this solution is equivalent to 0·01 milligram of chlorine. About 30 grams of stannous chloride are dissolved in water freely acidified with hydrochloric acid, and the solution is likewise diluted to 1 litre. To ascertain the strength of the stannous solution, 10 c.c. are taken with a pipette, diluted with distilled water and 5 c.c. of hydrochloric acid; a few drops of solution of potassium iodide and starch paste are added; and the standard solution of dichromate is run in from a burette, until a blue colour is produced by the liberation of iodine. If 20 c.c. of the standard dichromate solution are required, 1 c.c. of the stannous solution will equal 2 c.c. of the former, and also 0·02 milligram of chlorine.

Again, supposing the tin solutions to be of the above strength, 20 c.c. of the new standardised solution are measured as before, diluted with water, and 1 gram of bleaching powder well triturated with water is added, together with 10 or 12 c.c. of hydrochloric acid. The reaction is energetic and complete, and if a sufficient amount of hydrochloric acid is introduced, the solution will become perfectly clear.

A few drops of solutions of starch and potassium iodide are now added, and afterwards standard dichromate solution, until the deep blue colour of iodide of starch remains permanent. Supposing that 10 c.c. of the latter solution are consumed, then  $10 \text{ c.c.} \div 2 = 5 \text{ c.c.}$ ;  $20 \text{ c.c.} - 5 \text{ c.c.} = 15 \text{ c.c.}$  As 1 c.c. of the stannous solution equals 0·02 Cl. and 15 c.c. are required for 1 gram of bleaching powder, then  $15 \times 0·02 \text{ Cl.} = 0·030 \text{ Cl.} = 30 \text{ per cent.}$

Herreshoff objects to Penot's well-known arsenic method, upon the ground that, in the first place, it is difficult to ascertain the purity of the arsenious acid employed; and secondly, that the solution of sodium arsenite will not remain with certainty unchanged for any length of time. In the present instance, although the tin solution alters slowly by keeping, it is nevertheless a matter of a few moments only to re-standardise it accurately by means of the dichromate solution.

The process, however, is not free from an objection which is sometimes urged against Bunsen's method, viz., that many specimens of bleaching powder contain chlorate, which, liberating chlorine on the addition of hydrochloric acid, will consume a certain volume of standard solution, and thus raise the percentage. Penot's method is not liable to this source of error.

Another method is given by Graeger (*Dingl. polyt. J.* cci. 167), depending on the use of ferrous sulphate.

To a dilute and strongly acidified solution of ferrous sulphate, the strength of which is exactly fixed by a  $\frac{1}{10}$ th potassium permanganate solution, the bleaching powder solution is added with a pipette, the point of the latter being placed close on the bottom of the vessel, so that the bleaching powder solution forms the lower layer of liquid; the glass stopper is placed in the flask, and the latter, with its contents, is well shaken, and then allowed to stand for some minutes. When a sufficient quantity of ferrous sulphate is used, scarcely any smell of chlorine—in most cases, none at all—is perceived on opening the flask. The excess of the ferrous salt is now estimated with the  $\frac{1}{10}$ th permanganate solution, the difference between this and the original amount of ferrous salt used representing the weight oxidised by the hypochlorous acid, from which the available chlorine in the powder is readily calculated. If 1 gram of bleaching powder be fixed as the constant weight to be taken, a sufficient excess of iron salt must be added to absorb all the oxygen yielded, and to leave not too large a residue to be estimated by the permanganate solution. 4 or 5 grams of ferrous sulphate is recommended as the weight to be used. The results are found to correspond exactly with those obtained by the use of Penot's solution of sodium arsenite. Graeger does not recommend the use of ammonio-ferrous sulphate as a substitute for ferrous sulphate, since it gives use to the formation of nitrogen chloride, as previously shown by Biltz.

Calvert (*Compt. rend.* lxxv. 411) analyses bleaching powder by exhausting a known weight of it with water, treating the filtrate with carbonic acid, and boiling to decompose bicarbonate. The precipitated calcium carbonate represents the quantity of hypochlorite, while the calcium chloride remains in solution, and may be determined by silver nitrate or by evaporation to dryness, and fusion. The average results give 1 part hypochlorite to 2 of chloride.

**BLEGIOOLITE.** This name is given to an iron colite belonging to the brown Jurassic formation of the Alps from the Glarnisch, in the Canton Glarus. It possesses a general interest, in so far as its formation by deposition from an ancient Jura Sea admits of chemical demonstration. When the iron-ore is exhausted with water, the resulting solution is found to contain the constituents of sea-water, viz., small but distinctly recognisable quantities of chlorine (bromine, iodine), magnesia, and alkalis. Specimens taken from the very middle of the compact mass contained these soluble

constituents, showing that they could not have been introduced by subsequent infiltration, but must have been derived from particles of sea-water mechanically enclosed in the mass as it was deposited. The quantity of chlorine found was 0.034 p.c. (A. Baltier, *Deut. Chem. Ges. Ber.* v. 983).

**BLENDE, ZnS.**—This mineral occurs at Unkel in rhombic dodecahedrons, sometimes of considerable size, and having their faces thickly covered with smaller blende crystals, all disposed parallel to one another, so that the reflected images from their dodecahedral faces coincide with those from the faces of the large crystal. The small crystals are very irregularly developed, but exhibit the face 303 in combination with  $\infty O$ , forming a four-faced accumulation of its octohedral summits, by which it is easy to recognise the situation of the faces of the crystal. The occurrence of 303, and of the subordinate faces  $\infty O \infty$  and  $O$ , marks out the independent form of the small crystals, showing that the faces of the large crystal have not been corroded, but are covered with a layer of smaller crystals in regular order (A. v. Lasaulx, *Jahrbuch f. Mineralogie*, 1871, 937).

**BLOOD. Inorganic Constituents.**—Analyses of the inorganic constituents of dogs' blood have been made by Jarisch (*Ann. Ch. Pharm.* clxiii. 236). The blood was received direct from the vessel in carefully weighed and stoppered flasks surrounded by ice in order to avoid loss by evaporation. The weight was accurately determined after the blood had been allowed to thaw. The blood was then evaporated, and the mass, before complete incineration, digested with hot water in order to extract soluble chlorides, &c., and thus provide against loss of those constituents by strong heat. The solution was evaporated, incinerated to destroy organic matters, and redissolved in water. This solution was added to the fully incinerated mass, and the whole evaporated and dried. In this manner the inorganic constituents were obtained without loss. As, however, even after the most careful incineration, it is almost impossible to get rid of all the carbon, the results are always a little too high, but serious error is eliminated by comparison of the found with the calculated constituents.

The ash so obtained is partly soluble in water, and completely so in hydrochloric acid. The watery solution has an alkaline reaction.

The following Table contains the percentage results of four analyses of blood-ash, three of arterial and one of venous blood, compared with those formerly obtained by Verdeil:—

	Arterial Blood			Venous Blood	Verdeil	
	I	II	III	IV	A	B
Phosphoric anhydride	13.44	11.84	13.00	11.02	13.96	11.69
Sulphuric anhydride .	4.08	4.72	3.28	3.97	1.71	1.08
Chlorine .	30.55	33.73	30.08	30.48	30.25	30.94
Carbonic anhydride .	—	—	—	—	0.53	0.37
Potash .	4.43	3.54	3.66	3.70	15.16	19.16
Soda .	41.00	44.73	40.48	41.81	32.19	29.03
Lime .	1.01	1.61	1.25	1.13	1.10	0.70
Magnesia .	0.70	0.75	0.64	0.41	0.67	4.38
Ferric oxide .	9.14	6.68	7.56	10.08	12.75	8.65

Jarisch's results agree in many points with those of Verdeil; but he finds no carbonic acid, and his percentages of soda are much higher, and those of potash lower than in Verdeil's analyses. The quantities of phosphoric acid, chlorine, lime, and magnesia, and ferric oxide, differ but little.\*

The following are the mean percentages of the various constituents calculated from Jarisch's four analyses:—

\* In a note to Jarisch's paper, Liebig remarks: "The differences in the determinations of potash and soda are doubtless due to the varying amounts of the two alkalis in the blood. Blood of oxen slaughtered here (at Munich) gave by dialysis sodium chloride and an abundance of potassium salts; the concentrated liquid effluoresced with acids and contained a small quantity of phosphate of alkali-metal."

	In 100 parts of Ash	In 100 parts of fresh Blood
Phosphoric anhydride . . . . .	12.32	0.1103
Sulphuric anhydride . . . . .	4.01	0.0358
Chlorine . . . . .	31.43	0.2805
Potash . . . . .	3.83	0.0342
Soda . . . . .	42.01	0.3748
Lime . . . . .	1.25	0.0112
Magnesia . . . . .	0.65	0.0058
Ferric oxide . . . . .	8.34	0.0948

Total amount of Ash in fresh Blood.

Calculated	Found
0.8640	0.8922

**Dissolved Earths and Phosphoric Acid in Alkaline Blood.**—The existence in the blood of earthy phosphates combined with albumin, and thereby kept in solution, has often been assumed, but the earthy albuminates have not hitherto been actually prepared. Fokker, however (*Pflüger's Archiv*, vii. 274), has obtained the albuminates of lime and magnesia by leaving a mixture of albumin with the earth to stand for several hours. Lime-albuminate is most easily prepared by placing filtered white-of-egg in a shallow basin, placing a piece of filter paper on the surface, and strewing pounded lime on it. In a few days a translucent gelatinous layer of lime-albuminate forms on the under side of the paper. Lime albuminate is soluble in water, in solution of sodium chloride, and in phosphoric acid. Its aqueous solutions are not coagulated by boiling, except after the addition of neutral salts. They are precipitated by acids, the precipitate being soluble in excess. Magnesia albuminate is soft, slimy, and much more soluble in water than the lime-compound.

When an aqueous solution of lime-albuminate is precipitated by carbonic acid, the precipitate dissolved by sodium carbonate, and sodium phosphate added to it, a clear sometimes opalescent fluid is obtained, which will remain for many days unchanged, and has a strongly alkaline reaction. It contains lime, which can be precipitated by ammonium oxalate. The alkaline reaction of the liquid shows that the lime is not present as phosphate, and the fact that the solution may be boiled or kept several days *in vacuo* without becoming turbid shows that the lime is not present as carbonate dissolved in excess of carbonic acid. It is present as *lime-phosphate-albuminate*. The alkaline reaction can be due only to alkaline carbonates (or phosphates). The addition of free alkali causes a precipitate of calcium phosphate. If a solution of lime-albuminate is mixed with sodium phosphate, the phosphoric acid combines with the lime, and soda, which again destroys the newly-formed compound, is set free; but if the lime-albuminate is first precipitated by an acid and sodium phosphate then added, the acid used in the precipitation neutralises the soda, which is set free, and the lime-phosphate-albuminate remains in solution.

That lime-albuminate is present in blood is shown by the fact that serum behaves exactly like solutions of lime-albuminate, *i.e.* it can be preserved for some time *in vacuo* without depositing calcium phosphate; but this is gradually thrown down by caustic alkalis and precipitated by ammonium oxalate. The serum must be much diluted before the caustic alkali is added, as an albuminate is otherwise apt to form which interferes with the deposition of the precipitate.

It is probable that all the lime in the serum is present as lime-albuminate, and that no other lime-compounds exist in the blood.

**Iron in the Blood of an Invertebrate Animal.**—The blood of the *Limax flava* is almost colourless, and contains numerous elliptical corpuscles, about the size of the blood-corpuscles in the cow. It has an alkaline reaction, and consists of water 96.095 p. c., dry residue 3.905, ash 0.767, and iron, reckoned in the metallic state, 0.00069 p. c. Now if iron really forms a constituent of the blood of the snail, it may be expected that, as in the higher animals, it will be present in the blood in larger proportion than in the muscles. At first sight it would appear not to be so, for the snail, freed from its intestines, contains water 84.88, dry residue 15.12, ash 3, and iron 0.001176 p. c., a quantity of iron larger than that in the blood. This is due to the greater proportion of solid residue in the muscles; and when equal quantities of the dry residue of muscle and of blood are compared, the latter is found to contain more than twice as much iron as the former, the numbers being 0.0177 p. c. of iron in dried blood, and 0.0078 in dried muscle. This proportion is very much smaller than in animals with red blood, the dried blood of the ox containing ten times as much iron as the dried muscle. The actual amount of iron in the blood of the limax is only  $\frac{1}{10}$  of that in red blood. The colourless character of the blood is due to the absence of

hæmoglobin, or to the presence of an analogous substance in small quantity only, since the blood remains yellowish, and does not acquire a red tint even when concentrated by evaporation (Boussingault, *Compt. rend.* lxxv. 173).

*Action of Carbon monoxide on the Blood-globules.*—Cl. Bernard (*J. Pharm.* [4] xiii. 255) recommends the displacement of oxygen from blood by carbon monoxide (1st *Suppl.* 354), as a method of collecting the gases of blood for analysis. The blood is drawn from a vein or artery, as the case may be, by means of a graduated syringe, into which a volume of carbon monoxide equal to that of the blood to be analysed has been previously introduced; this prevents access of air, and formation of carbon dioxide. The blood is agitated to facilitate the combination of the carbon monoxide and hæmoglobin, and then introduced into a glass globe in which a vacuum has been previously made by means of a mercurial pump.

The gases of the blood are then evolved, and may be submitted to analysis in the ordinary way. In an experiment thus conducted it was found that arterial blood, on its entrance into the muscle of a dog's thigh, contained 7.31 p. c. by volume of oxygen, whilst the venous blood of the same muscle contained only 5 volumes, 2.31 vols. having therefore disappeared in the muscle.

To detect the presence of carbon monoxide in an apartment, Bernard recommends the spectroscopic examination of the blood of an animal which has been kept in it (See further, *Chem. Soc. J.* [2] ix. 839).

*Quantity of Ammonia evolved from Blood by Potash and by Permanganates.*—Blood yields about one-fifth as much ammonia to potash as to potassium permanganate. 100 c.c. of sheep's blood heated to 150° with potash give off 0.46 gram of ammonia, and the residue heated with permanganate yields 2.20 grams of ammonia (Wanklyn, *Chem. Soc. J.* [2] x. 646).

*Separation of the Colouring Matter of Blood by Solution of Tannin.*—Traces of blood in urine and other liquids may be detected by adding ammonia or potash, then a solution of tannin, and lastly acetic acid to slight acidulation. If blood is present, a dark coloured precipitate immediately forms, which after treatment with sal-ammoniac and glacial acetic acid, yields splendid crystals of hæmatin (H. Struve, *Zeitschr. anal. Chem.* xi. 29).

*Influence of Quinine on the process of Oxidation in the Blood.* (A. Schulte, *N. Rep. Pharm.* xx. 539).—Quinine is known to exert great power in arresting the processes of fermentation and putrefaction, and to act as a powerful poison on the lower organisms, or to speak more generally, on all moving bodies consisting of protoplasm. It kills the fungi, bacteria, &c. which accompany fermentation and putrefaction, and puts a stop to those processes themselves. It arrests the motion of the white blood-corpuscles, and thus prevents them from making their exit from the blood-vessels. It therefore diminishes or arrests the formation of pus in inflammation, pus consisting in great measure of an accumulation of white corpuscles which have issued from the vessels. It destroys the power of certain substances to produce ozone, and amongst others, of the red blood-corpuscles: hence when present in the blood, it retards the change of tissue, and thereby lessens the production of heat. It has indeed been shown by Ranke and Kerner that the amount of uric acid and urea excreted in the urine is greatly diminished by large doses of quinine. It remains a question, however, how much of this effect is due to the direct action of quinine on oxidation, and how much to its indirect influence through the nervous system. The former view is supported by an observation of Harley, who found that blood to which quinine had been added, in the proportion of 1 part to 12,000, took up less oxygen and gave off less carbonic acid than normal blood.

The most convenient method of investigating this question of oxidation, is to observe the changes in the alkalinity of the blood. Zuntz noticed that a considerable formation of acid begins to take place in blood immediately after it is drawn, and continues in a lesser degree till putrefaction begins. The amount of acid formed was estimated by the diminution it produced in the alkalinity. The process employed for this purpose depends upon the fact that the colouring matter of blood-corpuscles does not diffuse out of them into sufficiently concentrated solutions of sodium chloride, while the alkalis or salts contained in the corpuscles diffuse readily.

The alkalinity was determined by means of dilute phosphoric acid to which a quantity of sodium chloride had been added, sufficient to prevent the solution of the blood-corpuscles and the consequent interference of their colouring matter with the reaction. The point of saturation was considered to be reached when a distinct reddening of blue litmus-paper was produced, even though the red disappeared immediately. This transient reddening by carbonic acid was chosen rather than the first permanent reddening, because it could be more easily observed. This mode of observation does not give the

absolute amount of alkalinity, but the comparative amount in different samples of blood is all that is wanted; and if they be treated alike as regards temperature, and agitation, &c., the error caused by the carbonic acid is the same in all. The amount of error may be approximately estimated by noting the point at which a transient reddening occurs in the cold solution of sodium carbonate of nearly the same alkalinity as the blood, and then determining the real alkalinity of the boiling solution.

By this mode of observation, Zuntz and Scharrenbroich found that quinine and berberine lessen the production of acid; and this result is confirmed by A. Schulte (*N. Rep. Pharm.* xx. 639), whose experiments show that quinine can stop the formation of acid, both before and after the conglutination of the blood; also that sodium picrate has a similar action to that of quinine, and is nearly as powerful, while cinchonine has a very much smaller effect. Harley found that while quinine lessened oxidation in the blood, other substances, such as snake-poison, increased it. It would seem also, from the experiment of Binz, that similar processes occur in the living body; for when putrid fluids were injected into the circulation of an animal, its temperature rose, but if these fluids were previously mixed with quinine, or if a dose of quinine was injected simultaneously with them, the rise of temperature was arrested or much diminished. Zuntz, to determine the influence of quinine on tissue-change, and the excretion of urea, put himself on a constant diet, and after the daily amount of urea excreted had become constant, took three doses of 0.6 gram of quinine hydrochloride, for two days. The amount of urine at first increased by a third, and then diminished by a corresponding amount. The specific gravity sank from 1.018 to 1.012, the urea sank one-third on the first day on which quinine was taken, and was still further diminished on the second. As soon as the quinine was stopped, the urea increased, and reached its normal amount on the fifth day.

According to Kerner, (*Pflüger's Archiv.* iv. 27) quinine puts a stop to the motions of the white blood-corpuscles, and renders them round and darkly granulated. This action is not due, as Stricker and others have supposed, to the presence of free acid, inasmuch as perfectly neutral hydrochloride or carbonate of quinine in the proportion of 1 part to 400 of fluid, produces this effect, either in aqueous or in alcoholic solution. Solutions of salicin, caffeine, atropine, and sodium arsenite in a similar state of concentration have little or no effect.

On the Composition of the Blood in Chyluria, see Hoppe-Seyler (*Med.-Chem. Untersuchungen*, 1872, 551; *Chem. Soc. J.* [2] ix. 740).—On the Blood and Urine in Leukæmia, see Reichardt, *Arch. Pharm.* [2] cxlv. 142; *Chem. Soc. J.* [2] ix. 421.

**Hæmoglobin.**—Important observations on the presence of this substance in the muscles of Mollusca, and on its distribution in the living organism, have been made by E. Ray Lankester (*Pflüger's Archiv. f. Physiologie*, iv. 315).

The pharynx of the gasteropods is red, and in *Limæus* and *Paludina* the colour is due to hæmoglobin; this is proved by the spectroscopic appearances and changes. Perhaps as other gasteropods have their pharynges of a red colour, this is in all cases produced by hæmoglobin. The blood of the above and other gasteropods contains, however, no hæmoglobin, and is, in fact, colourless. The only mollusc in which hæmoglobin has been found is *Planorbis* and the allied species, in which the blood is of a brilliant red colour.

The hæmoglobin is distributed through the pale yellow muscular tissue of the pharynx of *Limæus*, and highly refractile granules are also seen. These are apparently identical with the pigment-granules surrounding the ganglion-cells which encompass the nerve-centres, and are of a brilliant yellow or orange colour. The same granular masses are met with in the salivary glands. This yellow pigment gave no distinct absorption-bands, yet the œsophageal ganglia appeared to contain hæmoglobin. It is possible that the yellow granules stand in relation to the development of the hæmoglobin in the muscular tissue, or that occasionally they may become impregnated with hæmoglobin. It is to be expected that the manner in which hæmoglobin is formed in these animals, and the form in which it exists in their muscles, will throw light upon the formation of hæmoglobin in the blood-globules of the Vertebrata.

These observations indicate that the province of hæmoglobin in the animal kingdom is a wide one, and is closely related to the activity of the muscular tissue. It cannot be supposed that the presence of hæmoglobin in the muscles in the above cases is casual. The presence of hæmoglobin in the pharynx muscles of the gasteropods is in accordance with the observation previously made by Lankester, that in all cases the most active and powerful muscles are furnished with hæmoglobin. In keeping with these facts also is the observation, that whilst in man the unstriped muscular fibres of the alimentary canal is free from hæmoglobin, the smooth fibres in the rectum are provided with that substance.

*Distribution of Hæmoglobin in various Organisms.*—Hæmoglobin has been detected

in the following cases by means of the spectroscope:—1. In the blood of the vertebrata the hæmoglobin is located in the red corpuscles. In *Amphioxus* it is found in the plasma, and not in the corpuscles. 2. In most of the striped muscles of mammalia and birds; but only in the cardiac muscles, and in certain very active muscles of other vertebrata. 3. In the unstriped muscle in the human rectum; in other unstriped muscles it is mostly absent. 4. Its presence in the *Annelida* is variable; in some of these it is accompanied by a second dichroic substance very like hæmoglobin in its spectroscopic relations. 5. It is present in the fluid from the perivisceral cavity of the leech. 6. Hæmoglobin is distributed through the plasma of the so-called blood of the larva of *Chironomus*; but it has been sought in vain in other insects, myriapods, and arachnida. 7. It is also present in the blood-plasma of certain crustaceans, whilst in others it is absent. 8. It is, for the most part, absent from the blood of the molluscs, though it is present in the blood of a gastropod—viz. *Planorbis*. 9. Hæmoglobin is met with in the muscular fibres from the pharynx of gastropod molluscs, as *Limnaeus* and *Paludina*, whilst it is wanting in their blood. 10. There is perhaps some connection between hæmoglobin (which is not met with in plants) and chlorophylloid bodies.

*Compound of Hæmoglobin with Carbon monoxide. Carboxy-hæmoglobin* (1st Suppl. 354).—Some discussion has arisen as to the manner in which carbon monoxide is united to hæmoglobin, and as to whether the resulting compound is a fixed compound or not. Donders (*Pflüger's Archiv*. iv. 28) states that carbon-monoxide may be expelled from blood saturated with it, by oxygen, carbon dioxide, and hydrogen, even at 0°; oxygen does not convert the monoxide into dioxide, but simply drives it out. If this be the case, it should be possible to pump the carbon monoxide out of blood saturated with it, although it may not be removed quite so easily as oxygen.

The possibility of this, though denied by Rawrocki and Pokrowsky, appears to be established by the experiments of Zuntz (*ibid.* v. 584). When blood saturated with carbon monoxide was placed in a receiver connected with an exhausting pump, and warmed to 37°–42°, an active escape of gas took place, ceasing apparently at the end of half an hour. When, however, the pumping was continued at various intervals, fresh quantities of gas were given off, and a further quantity was obtained by heating the receiver to 60°. The blood so exhausted was found to give the spectrum of reduced hæmoglobin, which was replaced by the spectrum of oxy-hæmoglobin after standing in the air. The hæmoglobin had not undergone decomposition, two analyses giving exactly the same results. The gas obtained was freed from carbon dioxide by caustic potash and from oxygen by potassium pyrogallate. The oxygen obtained, derived in all probability from the air, does not give rise to formation of carbon monoxide.

The gas obtained at 60° was analysed separately from that at 40°. From 31·65 c. c. of dogs' blood, sp. gr. 1071, the quantities were—

at 40° C. — 4·607 c. c. CO (0° and 1 m.)

at 60° C. — 0·998 c. c. CO

Total = 5·605 c. c. CO

i.e., = 17·7 p. c. of the blood-volume.

These experiments demonstrate the important fact that the gas cannot be pumped out all at once, but only at intervals. Schöffner (*Centralbl. f. d. medicin. Wissenschaft*, 1866, No. 42) found that this was also true of carbon dioxide, and he attributed the result to the progressive development of an acid in the blood, by which the gas was set free. Zuntz, however, shows that this supposition is untenable, because he finds that a solution of sodium bicarbonate similarly treated gives off carbon dioxide in the same fitful manner, though the effect cannot in this case be attributed to the gradual development of an acid. Moreover, the total quantity of carbon monoxide obtained agrees with that which was previously dissolved in the blood, whereas if its evolution were due to progressive decomposition, the quantity evolved should be greater.

The preceding results sufficiently account for the fact that other investigators were unable to extract carbon monoxide from the blood by exhaustion, inasmuch as the process was supposed to be complete when no more gas was evolved after the first pumping. They must also modify received ideas regarding poisoning by charcoal fumes. It need no longer be supposed that carbon monoxide cannot be removed from the blood, except by oxidation to dioxide. So long as the heart still beats, there is hope of restoring the blood to its normal condition by energetic artificial respiration.

According to Podolinski (*Pflüger's Archiv*. vi. 568) blood saturated with carbon monoxide is completely deprived of that gas by agitation for half an hour with hydrogen, and more rapidly by oxygen. Nitrogen dioxide absorbed by blood, is

likewise expelled by hydrogen, but less rapidly than carbon monoxide. Hence it appears that the compounds of hæmoglobin with carbon monoxide and nitrogen dioxide are similar in character to oxy-hæmoglobin: the order of stability being, oxy-hæmoglobin, carboxy-hæmoglobin, nitroso-hæmoglobin. Each of the three gases, O, CO, NO, can be expelled by the one immediately following, and each also more easily by the one immediately preceding, than by any other indifferent gas.

According to Keschlakoff and Bogomoloff (*Zeitschr. anal. Chem.* viii. 228) solutions of oxy-hæmoglobin and carboxy-hæmoglobin, through which ammonia is passed gradually, turn brownish-green and no longer exhibit any absorption-bands. Arsine colours solutions of oxy-hæmoglobin, first yellow-brown, then green-brown, the absorption-bands gradually disappearing and being replaced by the band of reduced hæmoglobin, whereupon the solution becomes somewhat red; on the next day, however, the last-mentioned band disappears. Carboxy-hæmoglobin is coloured dingy green by arsine, and its absorption-bands are destroyed.

*Absorption of Oxygen by the Blood.*—*Estimation of Hæmoglobin.* From experiments made by N. Gréhant (*Compt. rend.* lxxv. 495) it appears that normal arterial blood does not contain as much oxygen as it can take up. The amount obtained from blood from the carotid of a dog under ordinary circumstances was 16.3 volumes p. c.; after the inhalation of oxygen this rose to 23.3 p. c., but blood from the same animal saturated with oxygen by agitation contained 26.8 p. c. The quotient  $\frac{26.8}{16.3}$  evidently depends on the rapidity of the circulation through the lungs, the healthy condition of these organs, the activity of the respiratory movements, &c. Thus the relation of the volume of oxygen actually contained in arterial blood to the maximum quantity which it can absorb represents with tolerable exactness the effect produced by the respiratory efforts.

The amount of oxygen absorbed by specimens of blood from different animals of the same species varies with the amount of hæmoglobin they contain, and the quantity of oxygen absorbed affords a ready method of estimating the hæmoglobin. As part of the oxygen, however, is taken up by the salts of the blood and dissolved in the serum, it is better to use carbon monoxide, which is absorbed to a somewhat smaller extent than oxygen, and indicates the amount of hæmoglobin more exactly. Some experiments made by this method seem to show that hæmoglobin is destroyed in the liver.

*Influence of Acids upon the Oxygen of Hæmoglobin.*—Lothar Meyer observed that the addition of tartaric acid to the blood caused a large proportion of the oxygen contained in it to disappear. This observation has been confirmed by Pflüger and Zuntz, who find that phosphoric acid exerts a similar action, which they attribute to the splitting up of the hæmoglobin by the acid, and the subsequent oxidation of one of the products of its decomposition at the expense of the oxygen in the blood. These experiments have been continued, under Pflüger's directions, by G. Strassburg, who finds that the addition of phosphoric acid to chemically pure hæmoglobin suspended in water, or dissolved in sodium carbonate, causes oxygen to disappear from it in the same manner as from blood. The amount of oxygen loosely combined with dry hæmoglobin at 0° and 1 meter pressure appears from these experiments to be from 0.4483 to 0.8852 c.c. to 1 gram of hæmoglobin, instead of 1.277 c.c. as found by Preyer. The variation in the amount seems to show that oxidation takes place in solutions of hæmoglobin saturated with oxygen, and that part of the oxygen consequently disappears during the process of pumping out the gases of the blood (*Pflüger's Archiv*, iv. 454).

*Oxidising Power of the Blood.* Schützenberger a. Risler (*Compt. rend.* lxxvi. 440) determine the quantity of oxygen contained in blood by means of a standard solution of sodium hyposulphite  $\text{Na}_2\text{S}_2\text{O}_3$  (1st Suppl. 1063) added in sufficient quantity to absorb immediately all the available oxygen; the excess of hyposulphite added is afterwards determined by its power of decolorising a solution of indigo-carmine.

The strength of the hyposulphite solution is previously determined with reference to an ammoniacal solution of copper containing 4.46 grams of cupric sulphate per litre, 10 c. c. of which, when decolorised by the hyposulphite, yield 1 c. c. of oxygen. The hyposulphite solution should be equivalent to about an equal volume of the cupric solution, and to three times its volume of the indigo solution. When the hyposulphite is oxidised by free oxygen, it is converted into sulphate,  $\text{Na}_2\text{S}_2\text{O}_4$ , each atom of oxygen oxidising 1 mol. of the hyposulphite; but when it is oxidised by the ammoniacal cupric solution, 1 atom of oxygen oxidises 2 mol. of the hyposulphite, probably converting it into an acid of the polythionic series.

The estimation of the oxygen in blood is made by means of a three-necked bottle having the capacity of a litre. Into the middle aperture are fitted, by means of a



caoutchouc stopper, two Mohr's burettes, one containing the hyposulphite solution and the other the indigo. The two other apertures serve for the entrance and exit of a current of hydrogen gas, and for introducing the other liquids by means of a tap-funnel.

Into this vessel are introduced, a half litre of spring water (containing free oxygen); 50 c.c. of water holding in suspension 5 grams of kaolin (which renders the water opaque and makes the changes of tint visible, in spite of the colour of the blood); a small quantity of indigo-carmin; and, lastly, by means of another burette, a quantity of the hyposulphite solution sufficient to absorb the oxygen and decolorise the indigo. The bottle being then closed, the air is expelled by a stream of hydrogen; and by introducing, first, a small quantity of the hyposulphite, then of indigo-carmin, a point is easily found at which the liquid contains neither oxygen nor hyposulphite in excess. 50 c.c. of hyposulphite are now introduced; then by means of the funnel, 5 c.c. of blood; the liquid is shaken, and the indigo-solution allowed to run in drop by drop, till the liquid just acquires a permanent violet tint. Lastly, the volume of hyposulphite equivalent to that of the indigo employed is deducted from the 50 c.c. of hyposulphite, and the quantity of oxygen corresponding with this difference is determined by calculation.

Schützenberger and Risler have hitherto experimented only on ox-blood or dog-blood saturated with oxygen, and with the same blood deoxidised with the air-pump or by carbon monoxide. The general results of their observations are as follow:—

If the oxyhemoglobin of the blood acted on the hyposulphite in the same manner as free oxygen, a minimum of 88 to 90 c.c. of oxygen should be found for 100 c.c. of ox-blood agitated in contact with the air, and a minimum of 50 to 52 c.c. of oxygen for 100 c.c. of blood deoxidised by the air-pump or by carbon monoxide. The difference is 38 to 40 c.c. Now the blood saturated with oxygen which was experimented on, yields to the pump only 19 c.c. for 100. It follows, therefore, that the oxygen of the blood acts on the hyposulphite, not like free oxygen, but like the combined oxygen of an ammoniacal cupric solution. The preceding numbers must therefore be divided by 2.

It appears then that blood saturated with oxygen possesses, with respect to the hyposulphite, an oxidising power equivalent to 45 c.c. of oxygen per cent.; and that blood deoxygenated by the pump or by carbon monoxide has an oxidising power equivalent to 25 or 26 c.c. of oxygen per cent. Blood saturated with oxygen by exposure to the air, or rather oxidised hæmoglobin, possesses therefore an oxidising power  $1\frac{1}{2}$  times as great as that which has hitherto been attributed to it according to the volume of oxygen separated by the pump or by carbon monoxide. This additional quantity of oxygen exists in a state of more intimate combination with the colouring matter, and cannot be removed except by chemical reducing agents.

A 10 per cent. solution of blood saturated with oxygen, and then mixed with excess of hyposulphite, exhibits the spectral line of reduced hæmoglobin, and becomes darker, its colour changing to red-violet. This reduced solution, after agitation with air, again yields by titration the same quantity of oxygen as before the reduction.

**Hæmatin and its derivatives.** (Hoppe-Seyler, *Medicinisch-chemische Untersuchungen*, 1871, 523).—Hæmatin contains, according to Hoppe's analysis, 60.91 to 61.18 p. c. carbon, 5.20 to 5.41 hydrogen, 8.63 nitrogen, and 8.68 to 8.83 iron. From these numbers he formerly deduced the formula  $C^{60}H^{5.2}N^{8.63}Fe^{8.68}O^{18}$  (1st Suppl. 355); but he has since proposed the formula  $C^{60}H^{5.2}N^{8.63}Fe^{8.68}O^{18}$ , which requires 64.35 C., 5.36 H., 8.83 N., and 8.83 Fe. This agrees nearly with the analytical results, so far as regards the hydrogen, nitrogen and iron, but differs greatly in the proportion of carbon it requires; which is more nearly that found by Mulder, viz. 64.63 to 65.01 p. c.

**Hæmatoporphyrin and Hæmatolin.**—When a solution of hæmatin in oil of vitriol is filtered through asbestos, a beautiful purple-red solution is obtained, which gives a small dark absorption-band just before the line D, and another very sharply defined band between D and E. When this solution is mixed with water, the greater part is precipitated, the precipitate being increased by addition of alkalis to neutralisation. The alkaline aqueous solutions of the precipitate are characterised by a faint band between C and D, a similar faint band between D and E, nearer D, a dark band in the same interval but nearer E, and lastly, a very dark band between E and F. This substance, *hæmatoporphyrin*, is free from iron, and gives by analysis 68.42 p. c. C., 9.58 N., 6.07 H., and 15.93 O., agreeing nearly with the formula  $C^{68}H^{6.1}N^{9.6}O^{16}$ , or  $C^{68}H^{6.1}N^{9.6}O^{16} \cdot 2H_2O$ , which requires 68.34 p. c. C., 9.38 N., 6.20 H., and 16.08 O. Its formation requires the presence of oxygen, and is represented by the equation:



When, on the other hand, hæmatin is acted upon by sulphuric acid in closed vessels,

*hæmatolin*  $C^{56}H^{70}N^{10}O^7$  is formed, which is but very slightly soluble in sulphuric acid, and very slightly soluble in caustic potash. Composition by analysis, 72.94 p. c. C., 10.02 N., 6.95 H., 10.09 O.; by calculation, 72.98 C., 10.02 N., 6.98 H., 10.02 O.

*Action of Reducing Agents on Hæmatin.*—Hæmatin offers considerable resistance to oxidising agents. It is, however, very sensitive to reducing agents, both in acid and alkaline solutions. By boiling a solution of hæmatin with caustic soda and pulverised zinc, as also by the action of sodium-amalgam on hæmatin in presence of water, reduction-products in great quantity are formed. They are all free from iron, but their separation is a matter of great difficulty. Their solution gives a complicated spectrum, with five absorption-bands. No exact analysis can be given.

*Tin and Hydrochloric Acid* act on hæmatin, in presence of alcohol, differently, according as the hæmatin is fully dissolved or not. When a concentrated solution, or one containing excess of hæmatin, is heated with tin or copper or zinc on the water-bath, a purple-red solution is formed, with, after a time, a resinous dark violet precipitate. The solution is characterised by two dark absorption-bands between D and E. When hæmatin, or hæmin crystals dissolved in alcohol containing sulphuric acid, are decomposed by hydrochloric acid and tin, and heated, a purple solution is formed, which also has a characteristic spectrum, viz., one band between D and E, another just before D, and another broad band between  $\delta$  and F, covering the latter line. When the evaporated solution is poured into boiling water, a brownish precipitate is formed, soluble in alcohol. This on evaporation yields a colouring matter, which in properties resembles the oxidised product obtained by distillation from the hæmatin reduced by zinc powder, and appears to consist of  $C^{54}H^{70}N^{10}ClO^7$ .

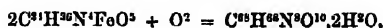
*Behaviour of Hæmatin when treated with Phosphorous Chloride containing free Phosphorus.*—When hæmin crystals are heated with this substance to a temperature of  $140^\circ$ , in closed tubes for 6-8 hours, a purple-brown fluid is formed, which gives a spectrum with three absorption-bands, one between C and D, close to C, a second between D and E—nearer E, and a third between  $\delta$  and F, beginning from  $\delta$ , and extending to the middle between  $\delta$  and F. No evolution of gas follows the opening of the tube. A crust forms on the sides, which, however, is easily separated. This substance is to a certain extent soluble in water, giving the same spectrum as hæmatoporphyrin. From the part insoluble in water a substance is obtained resembling hæmatin: it contains phosphorus, and gives by analysis, 52.67 p. c. C., 7.48 N., 5.11 H., 8.02 P., and 26.72 O.; hence its formula appears to be  $C^{56}H^{70}N^{10}P^2O^{12}$  or  $C^{56}H^{70}N^{10}O^{10}.4H^2PO^4$  (calc. 52.78 C., 7.24 N., 5.05 H., 8.02 P., and 26.91 O.). The agreement of the spectrum of this substance with that of hæmatoporphyrin seems to show that the latter consists of  $C^{56}H^{70}N^{10}O^{10}.2H^2O$ , or that it is a hydrate of the same molecule as that contained in the phosphorus-compound (Hoppe-Seyler, *Med.-chem. Unters.* 1871, 643).

*Action of Ammonia, Arsine, and Stibine.*—Alkaline solutions of hæmatin are coloured orange by ammonia, the absorption-bands become paler; a broad but diffuse shadow appears in the green part of the spectrum, and after some time, an amorphous precipitate falls to the bottom. This precipitate dissolves in acetic acid, and the solution exhibits the bands of acid hæmatin. When arsine is passed into an alkaline solution of hæmatin, the colour of the liquid gradually becomes red, and two of the absorption-bands of reduced hæmatin appear. Agitation with air restores the colour of the alkaline hæmatin, but after a few seconds, the solution begins quickly to redden, and this alternation may be repeated about ten times. If the passage of the arsine be longer continued, the alkaline solution turns brown, and sometimes deposits steel-grey crystals of arsenic on the following day. After this time, no more bands can be seen; nevertheless, the presence of hæmatin may be demonstrated by means of an ammoniacal solution of ferrous tartrate. The bands of reduced hæmatin may be recognised at a much greater degree of dilution than those of the alkaline or of the acid solution, a fact which seems to show that, in spite of the action of the arsine, part of the hæmatin has remained undecomposed. The action of stibine is the same as that of arsine (Koschlakoff a. Bogomoloff, *Zeitschr. anal. Chemie*, viii. 228).

*Hæmochromogen.*—From the most recent experiments of Hoppe-Seyler (*Med.-chem. Unters.* 1871, 523), it appears that hæmatin is not a direct product of the splitting up of hæmoglobin, but results from such a decomposition accompanied by oxidation. This oxidation takes place, however, so rapidly, that it is only by special precautions that the non-oxidised products can be obtained. When, however, a solution of hæmoglobin is reduced by hydrogen and decomposed by alcohol containing sulphuric acid or caustic potash, in an apparatus from which oxygen is completely excluded, a colouring matter is produced, which is acid, has a purple-red colour in alkaline solutions, and is characterised by certain definite absorption-bands. It is this substance, hæmochromogen, which yields hæmatin by oxidation. It has not yet been isolated or regenerated.

## BOILING POINTS OF HOMOLOGOUS COMPOUNDS. 203

by reduction of hæmatin, but its spectrum agrees generally with that of reduced hæmatin (p. 202). Hoppe-Seyler supposes it to have the composition  $C^{14}H^{16}N^4FeO^3$ , and represents the formation of hæmatin from it by the equation :



### BOILING POINTS OF HOMOLOGOUS ORGANIC COMPOUNDS.—

Kopp's well-known law, that the differences in boiling point between consecutive members of the same homologous series are equal, has been called in question by Linnemann (*Ann. Ch. Pharm.* clxii. 39), from whose experiments it appears that these consecutive differences are by no means equal, but exhibit considerable variation. The apparatus used by Linnemann for the fractional distillation of the several compounds and the determination of their boiling points is so contrived as to reduce to a minimum the errors arising from irregular boiling and from overheating (see DISTILLATION, FRACTIONAL). In twenty-five determinations thus made upon eleven different bodies (acids and ethers of the ethyl, propyl, and butyl series), the boiling points of different specimens of the same compound rarely differed from one another by so much as a tenth of a degree, the greatest and least differences observed (both in the case of normal butyl iodide) being  $0.3^\circ$  and  $0.02^\circ$ . This is sufficient to show that the method is susceptible of great accuracy.

The following Table exhibits Linnemann's determinations of the boiling points of a considerable number of compound ethers, &c., of the three groups above mentioned: the second columns giving the observed boiling points; the third the differences between them; and the fourth the differences of those differences, or differences of the second order:—

Chlorides				Bromides			Iodides		
	Boiling point	Difference	Decrease	Boiling point	Difference	Decrease	Boiling point	Difference	Decrease
Butyl . .	77.96	31.41		99.88	29.06		129.81	27.68	
Propyl . .	46.48	34.30	2.80	70.82	32.04	2.98	102.18	29.84	2.21
Ethyl . .	12.18			38.78			72.34		
Fatty alcohols				Fatty acids			Benzole ethers		
	Boiling point	Difference	Increase	Boiling point	Difference	Decrease	Boiling point	Difference	Decrease
Butyl . .	116.88	19.47		162.32	21.66		247.32	17.85	
Propyl . .	97.41	18.88	0.59	140.66	22.66	0.90	229.47	18.31	0.46
Ethyl . .	78.53			118.10			211.16		
Acetic ethers				Propionic ethers			Butyric ethers		
	Boiling point	Difference	Decrease	Boiling point	Difference	Decrease	Boiling point	Difference	Decrease
Butyl . .	124.30	22.32		145.99	23.65		164.77	21.35	
Propyl . .	101.98	24.98	2.66	122.44	28.64	0.09	148.42	22.35	1.00
Ethyl . .	77.00			98.82			121.07		
Ethyl ethers				Propyl ethers			Butyl ethers		
	Boiling point	Difference	Increase	Boiling point	Difference	Increase	Boiling point	Difference	Decrease
Butyrate .	121.06	22.26		143.42	20.98		164.77	18.78	
Propionate .	98.80	21.80	0.46	122.44	20.46	0.52	145.99	21.69	2.91
Acetate .	77.00			101.98			124.30		

## Boiling Points of Homologous Ethers.

Isomeric ethers, C <sup>n</sup> H <sup>2n+2</sup> O <sup>n</sup>			Isomeric ethers, C <sup>n</sup> H <sup>2n</sup> O <sup>n</sup>		
	Boiling point	Difference		Boiling point	Difference
Propyl acetate .	101.98	3.18	Butyl acetate .	124.30	1.86
Ethyl propionate .	98.80		Propyl propionate .	122.44	1.43
			Ethyl butyrate .	121.01	
Isomeric ethers, C <sup>n</sup> H <sup>2n</sup> O <sup>n</sup>					
				Boiling point	Difference
Butyl propionate . . . . .				145.99	2.57
Propyl butyrate . . . . .				143.42	

From these numbers Linnemann draws the following conclusions:—

1. Equal differences of boiling point in homologous series do *not* correspond with equal differences of composition.
2. In most of the series hitherto studied, the difference of boiling point increases as the amount of carbon becomes greater, at least in the lower terms of the series.
3. In many series, the differences of boiling point are nearly equal, in others they increase with increasing amount of carbon.
4. The isomeric ethers of the fatty alcohols and acids do *not* exhibit equal boiling points.

From these results, and from the close agreement already noticed between the observed boiling points of different samples of the same compound prepared by the preceding method, Linnemann infers that the *observed* boiling points coincide very nearly with the true boiling points, and consequently that the so-called 'calculated' boiling points can no longer be regarded as the true boiling points.

Pierre a. Puchot (*Compt. rend.* lxxv. 1440) have likewise compared the boiling points of a considerable number of compounds belonging to several homologous series, viz., alcohols, ethers and acids of the fatty group, and have come to the conclusion, that the difference between the boiling point of two consecutive terms of the same series is not constant, but subject to very considerable variation. As, however, those chemists take no account of the difference between normal and iso-compounds, it is impossible to know whether the compounds which they compared were really homologous. One point which they particularly notice is, that the boiling temperature of the propylic and butylic terms in each series of acids, ethers, &c., derived from the fermentation alcohols, is less than the difference between any two succeeding terms in the same series. Now, this is just what may be expected to follow from the fact that the propyl alcohol of fermentation is a normal alcohol, whereas all the higher fermentation alcohols that have been examined are iso-alcohols (see *Chem. Soc. J.* [2] xi. 268, 269).

**BOLETUS.** Many species of boletus become blue on exposure to the air after fresh fracture. By digesting *B. cyanescens* cut up into shreds with alcohol of 92 p. c. an extract is obtained which, after filtration, is brownish-yellow, then becomes green, and gives an intense indigo-blue colour with sodium hypochlorite; after concentration, it yields crystals of mannite, and the mother-liquor, treated with alcohol and ether, yields a golden-yellow solution, which leaves on evaporation a residue becoming deep green-brown with sodium hypochlorite.

The aqueous solution of the colouring matter has a strong acid reaction; hydrochloric acid does not change its brownish-yellow tint; neither does soda-ley, added to alkaline reaction; this, however, prevents the blue coloration with sodium hypochlorite from appearing. The colouring matter contains nitrogen, as, on heating it with caustic potash, ammoniacal vapours are given off; but it does not exhibit any reaction indicative of cyanides, or of aniline (as asserted by Phipson, *Chem. News*, xiv. 301), not giving the characteristic aniline reaction with hypochlorites.

The above-mentioned reactions with sodium hypochlorite have also been obtained, with the colouring matters similarly extracted, from *B. luridus*, *B. Satanas*, *B. Calopus*, and the brown-tubed variety of *B. variegatus* (H. Ludwig. *Arch. Pharm.* [3] calix. 107).

**BONE.** *Influence of Earthy Phosphates mixed with the Food on the Composition of the Bones.*—The experiments of J. Lehmann (*Ann. Ch. Pharm.* cviii. 357), v. Gohren (*Landwirth. Versuchs-Stationen*, iii. 181), and others have shown that calcium phosphate precipitated by ammonia from an acid solution, can be digested and assimilated by calves, sheep and other animals; and according to Hoppe-Seyler (*Med.-chem. Untersuchungen*, Heft II.), earthy phosphates added to human food are likewise absorbed, and increase the amount of earthy phosphates in the urine. These and other results have led to the idea that the ingestion of earthy phosphates may have some influence on the composition of the bones, and in fact the addition of earthy phosphates to fodder has been somewhat extensively practised.

Papillon (*Compt. rend.* lxxi. 372) fed a pigeon and two white rats for two months on food containing phosphates of strontium, aluminium and magnesium. The bone-ash of the pigeon was then found to contain 8.45 p. c. strontia and 0.66 magnesia, that of one of the rats, 6.95 alumina, and that of the other, 3.56 p. c. magnesia; the general conclusion from these experiments being that considerable quantities of the ingested earthy phosphates were deposited in the bones.

A contrary conclusion has, however, been arrived at by H. Weiske-Proskau (*Zeitschr. f. Biologie*, viii. 239), who made an extensive series of experiments of the same kind on young and old rabbits, but could not find the slightest trace of strontia, or any noteworthy increase of the magnesia, lime, or phosphoric acid in the bones when earthy phosphates were mixed with the food. The age of the animal has an influence on the composition of the bones, those of old rabbits containing more salts than those of young ones. The percentage composition of the bone-ash is much alike in both, but the proportion of magnesia seems to be somewhat higher, and of lime somewhat lower, in young animals. The percentage amount of phosphoric acid is almost the same in all bones, and is on an average 42.17 p. c.

The following Table exhibits the amount and composition of the ash of the bones, free from water and fat, of the animals subjected to the experiment. In the rabbits I—IX, the bones of all the four legs; in X and XI, the whole of the bones were taken for analysis:—

No.	Age	Kind of Salt added to the food	Ash p. c.	Lime p. c.	Magnesia p. c.	Phosphoric acid p. c.
I.	adult	Calcium phosphato	65.60	53.94	1.06	40.03
II.	6 months	" "	62.02	53.77	1.23	42.73
III.	adult	Magnesium phosphate	68.41	54.21	1.09	42.08
IV.	5 months	" "	61.99	53.68	1.24	42.01
V.	adult	Strontium phosphate	68.00	53.93	1.06	42.00
VI.	5 months	" "	62.30	53.60	1.23	42.67
VII.	adult	" No salt	67.87	54.16	1.09	42.02
VIII.	2½ months	" "	56.88	53.52	1.22	42.17
IX.	2½ months	Calcium phosphate	58.12	53.38	1.23	42.29
X.	4 weeks	" "	39.31	50.48	1.69	43.12
XI.	4 weeks	" No salt	38.58	51.99	1.51	42.65

*Iron in Bones?* According to some authorities, iron is a normal constituent of bone, whilst by others its occurrence in bone is attributed to the retention of colouring matter of the blood. The question has been further examined by Plugge (*Archiv. f. Physiologie*, iv. 101), who, to avoid the source of error just mentioned, macerated the bones in water till no residue was obtained on evaporation. Bones of various animals thus treated yielded not a trace of iron, whence it may be inferred that iron is not a constituent of bone, and that when it is found therein, its occurrence must be attributed either to retained blood, or to impurity in the reagents and vessels employed.

On the Solubility of the Phosphates of Bone-ash in Carbonic acid water, see PHOSPHATES.

On the determination of the relative age of fossil bones from the proportion of soluble and insoluble ossein contained in them, see A. Schenker-Kestner (*Compt. rend.* lxxix. 1207; *Chem. News*, xx. 311; *Jahresb.* 1860, 1249).—Objections against Schenker-Kestner's conclusion have been made by Elie de Beaumont (*Compt. rend.* lxxix. 1211). On the determination of the age of fossil bones from their chemical composition, see also Wibel (*Jahresb.* 1869, 1250).

**BORACITE.**—This mineral, hitherto found at Stassfurt only in microscopic crystals, has lately been obtained from the residues of the potassium chloride preparation in crystals of three varieties, viz.: 1. Small kidney-shaped druses consisting of an envelope of transparent greenish crystals about 0.5 mm. in shapo, enclosing a bluish or greenish grey microcrystalline nucleus composed of crystals of the same kind. 2. Small crystalline groups or nodules consisting of light green translucent to transparent crystals about 5 mm. long, enclosing a nucleus of white to greenish colour. 3. Larger druses in which a white, fine-grained nucleus of Stassfurtite gradually passes, towards the surface, into a greenish, fine-grained crystalline mass, surrounded wholly or partially by very small crystalline groups, and a few isolated crystals about 2 mm. in size.

All the crystals are well developed, and show no signs of efflorescence. They exhibit distinctly the combination  $\frac{O}{2} \cdot \infty O \infty \cdot \infty O$ ; in some specimens the face

$-\frac{O}{2}$  may be recognised with a lens; in a few the face  $-\frac{2O2}{2}$ . The tetrahedon is almost always predominant.

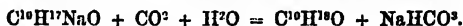
The crystals have a vitreous lustre, no distinct cleavage, a conchoidal fracture; hardness = 7; mean density = 2.91. They contain boric acid and magnesia, with small quantities of ferrous oxide and chlorino, from which, and from their morphological and physical characters, it is inferred that they consist of boracite,  $MgCl^{12} \cdot 2(3MgO \cdot 4B^2O^3)$ .

Stassfurtite, which has the same composition, and forms the nucleus of some of the boracite druses above mentioned (3), appears to be merely the cryptocrystalline form of boracite (B. Schultze, *Jahrbuch f. Mineralogie*, 1871. 844).

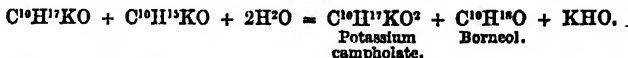
**BORNEOL**,  $C^{10}H^{18}O$ .—This compound is formed in small quantity by the action of alcoholic potash on camphor:  $C^{10}H^{18}O + H^2O = C^{10}H^{16}O + O$ , the nascent oxygen resinising part of the camphor (Bertholot, i. 626).—and in much larger quantity by acting on a solution of camphor in toluene with sodium, and treating the product with carbonic acid (Baubigny, 1st Suppl. 358):



and



If the camphor be dissolved in a petroleum oil of rather high boiling point, and potassium be used instead of sodium, potassium campholate and borneol are formed by the mutual action of the potassium-borneol and potassium-camphor first product; thus—



The natural borneol and that synthesized by the above two sets of reactions, exhibit respectively the rotatory powers,  $\alpha = +33.4^\circ$ ,  $44.9^\circ$ , and  $42.4^\circ$ .

Borneol treated with phosphorus pentachloride or hydrochloric acid yields a chloride  $C^{10}H^{17}Cl$ , which melts at  $132^\circ$ , and is converted into ordinary camphor by hypochlorous acid—



borneol itself is also converted into ordinary camphor by the same reagent:



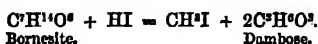
Bromine acts on borneol, forming first camphor and hydrobromic acid; and finally a mixture of monobromocamphor and borneol bromide. Phosphoric anhydride acts on borneol, forming a hydrocarbon,  $C^{10}H^{16}$  (the *borneene* of Pelouze), boiling at  $176^\circ$ – $180^\circ$ , and an isomeric condensation-product distilling at  $250^\circ$ – $280^\circ$ . Borneene smells like turpentine, but does not unite with hydrochloric acid or with hypochlorous acid (Kachler, *Ann. Ch. Pharm.* clxiv. 75).

Respecting the constitutional formula of borneol, see CAMPHOR.

**BORNESITE**,  $C^8H^{14}O^2$ .—(A. Girard, *Compt. rend.* lxxiii. 426).—A sweet volatile substance occurring in the caoutchouc of Borneo. It is crystalline, very soluble in water, slightly soluble in alcohol, melts at  $175^\circ$  without alteration, and, like dambonite (1st Suppl. 541), sublimes at  $205^\circ$  with slight decomposition. It does not ferment, neither does it reduce the potassio-tartrate of copper, but acquires the property of reducing this reagent by being boiled for several minutes with water.

slightly acidulated. Treated with a mixture of sulphuric and nitric acids, it forms a nitrated product, insoluble in water, soluble in alcohol, from which it is deposited in the crystallised state, melting at 30°–35°, and detonating loudly when struck.

Bornesite heated to 120° in a closed vessel with fuming hydriodic acid, decomposes, like dambonite, into methyl iodide and dambose:



Dambonite and dambose have no effect upon polarised light, but bornesite possesses a rotatory power of 32° to the right, or nearly half that of pure cane-sugar under similar circumstances. Dambonite and bornesite may be regarded as dambosates of methyl: dambonite =  $\text{C}^s\text{H}^n(\text{CH}^m)\text{O}^s$ ; bornesite =  $\text{C}^s\text{H}^n(\text{CH}^m)\text{O}^s$ .

**BORON.** Boric chloride,  $\text{BCl}_3$ , is easily prepared by heating finely powdered boric anhydride to 150° for three or four days in sealed tubes, with twice its weight of phosphorus pentachloride. The tubes must be well cooled before they are opened, and then warmed on a water-bath. Boric chloride then distils over, and a further quantity may be obtained by heating the white residue over the open fire. On heating to a higher temperature and finally to redness, there remains a white infusible mass, which is insoluble in water, and is resolved by prolonged boiling with water on alkalis, into boric and phosphoric acids. This body is probably identical with the compound of boric and phosphoric oxides described in the *First Supplement*, p. 360.

These experiments show that in the action of phosphorus pentachloride on boric oxide, there is formed, beside the trichloride, an oxychloride of boron, which does not give off the trichloride till heated above 100°. And, in fact, if the trioxide and trichloride of boron are heated together to 150° in molecular proportions, the contents of the tube are converted into a white gelatinous mass, which, when heated to 100° gives off half the boron chloride employed in the reaction. At a higher temperature, the white solid residue gives off an additional quantity of the chloride and leaves the trioxide. The reaction between phosphorus pentachloride and boric oxide is therefore that which is represented by the equation:



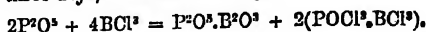
Phosphorus trichloride does not act on boric oxide even when heated with it for a fortnight to 200°. On the other hand, the bromochloride,  $\text{PCl}_2\text{Br}$ , acts readily on boric oxide, with formation of boric chloride and separation of bromine. Bromide of boron is not thereby produced, or at all events only in extremely small quantity. The tribromide, di-iodide and tri-iodide of phosphorus do not act on boric oxide. Boric chloride is not converted into the corresponding cyanide, either by cyanide of potassium, or by cyanide of silver.

Boric chloride may be distilled over sodium without decomposition; at 150° however a small quantity of boron is separated. Zinc-dust does not act upon it even at 200°. The chloride acts readily on bodies containing the radical HO or  $\text{NH}_2$ . A mixture of acetic acid and anhydride, treated with boric chloride, yields a crystalline compound, which is resolved by water into boric and acetic acids, hydrogen chloride and acetyl chloride being formed at the same time. By the action of boric chloride on the crude mixture of ethylamines (obtained by heating ethyl iodide with ammonia) a compound is obtained which melts when heated, then sublimes undecomposed, and if heated for a day to 200°, yields products of decomposition, among which are ethyl chloride and boron nitride (Gustavson, *Zeitschr. f. Chem.* [2] vi. 521).

**Boric Oxide, Acid, and Salts.** *Compound of Boric Oxide and Phosphoric Oxide.*  $\text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ .—When crystallised boric acid is heated to boiling in a platinum dish with concentrated aqueous phosphoric acid, the liquid first becomes milky, and then dries up to a white earthy mass, which when heated before the blowpipe, or even in a platinum crucible over a gas-flame fed by a blast of air, does not melt but retains its earthy character, merely becoming covered with an enamel-like crust when the phosphoric acid is in excess. This compound is not decomposed by water even at the boiling heat, and the excess of phosphoric acid may be removed from it by boiling water. It then contains boric and phosphoric oxides in equal number of molecules. Concentrated acids are without action upon it; caustic alkalis at the boiling heat dissolve it to a clear liquid. The pulverised substance heated with sodium yields sodium phosphide, together with a black scoriaceous substance, perhaps consisting of boron phosphide (A. Vogel, *Zeitschr. f. Chem.* vi. 125).

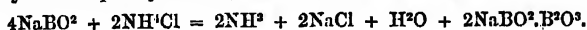
*Action of Phosphoric Oxychloride on Boric Oxide.*—When boric oxide is heated with phosphoric oxychloride in closed tubes, to 150°–170°, for eight or ten hours, a white

mass,  $\text{P}^2\text{O}^5 \cdot \text{B}^2\text{O}^3$ , is formed, whilst colourless crystals of a compound,  $\text{POCl}^3 \cdot \text{BCl}^3$ , sublime in the upper part of the tube. The latter melts in a closed tube at  $73^\circ$ , and when sublimed splits up into boric chloride and phosphoric oxychloride. Crystals of the chlorinated compound are also formed on passing the vapours of boric chloride into phosphoric oxychloride, and by heating boric chloride with phosphoric anhydride to  $200^\circ$  for two or three days, the reaction being:

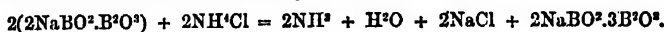


It is decomposed in contact with water, or by the moisture of the atmosphere, phosphoric acid, boric acid, and hydrochloric acid being formed. The white mass  $\text{P}^2\text{O}^5 \cdot \text{B}^2\text{O}^3$  is probably a mixture of phosphoric with boric anhydride, as it is resolved by water into phosphoric acid and boric acid, but if previously heated to redness it forms the insoluble compound  $\text{B}^2\text{O}^3 \cdot \text{P}^2\text{O}^5 = \text{PBO}^4$ , described by Vogel (Gustavson, *Deut. Chem. Ges. Ber.* iv. 975).

*Action of Borates on Ammonia Salts.*—This reaction, studied in 1848 by Bolley (*Ann. Ch. Pharm.* lxxviii. 123), has been further examined by R. C. Woodcock (*Chem. Soc. J.* [2] ix. 785). Bolley observed that free ammonia is evolved on mixing solutions of borax and sal-ammoniac containing equal numbers of molecules of the two; and that the solution when slowly evaporated, deposits crystals having the composition of a tetraborate  $\text{Na}^2\text{O} \cdot 4\text{B}^2\text{O}^3 + 10\text{H}^2\text{O}$  or  $2\text{NaBO}^2 \cdot 3\text{B}^2\text{O}^3 + 10\text{H}^2\text{O}$ ; also that an excess of sal-ammoniac converts the borax entirely into sodium chloride and boric acid. Woodcock finds that when 4 mol. of sodium metaborate  $\text{NaBO}^2$  (i. 645) are mixed with 2 mol. of sal-ammoniac, ammonia is copiously evolved, and the whole decomposes very rapidly and completely, leaving only the diborate (borax) and sodium chloride:



A mixture of commercial borax (3.57 grams) and sal-ammoniac (0.5 gram) dissolved in about 2 ounces of water and distilled, gave off the whole of the ammonia, leaving a residue of sodium chloride and Bolley's tetra-metaborate:



Borates either acid or normal may be advantageously employed for liberating ammonia from its salts, the action taking place neatly and perfectly and without frothing.

*Calcium Borate.*—This salt is found in the dried-up bed of a river on the Pampa of Tamarugal, near Tarapaca in Peru, and is collected by digging out the sand beneath the surface-crust of salt. It occurs in white nodules, having a shining, pearly, lamellar fracture, associated with yellowish prisms of glauberite, the whole being almost completely soluble in strong acids, but very slightly in water. It originates probably from the action of the acid emanations of the neighbouring volcano of Salgu on the calcium carbonate of the soil. It is a calcium diborate with 8 mol. of water,  $\text{CaO} \cdot 2\text{B}^2\text{O}^3 + 8\text{aq.}$  mixed with varying quantities of glauberite, sodium chloride, silica, alumina, and iron. The boric anhydride averages 17 p.c. (Thiercelin, *Bull. Soc. Chim. de Paris* [2] xvii. 387).

On the heat evolved in the combination of boric acid with ammonia, see **HEAT OF COMBINATION**.

*Boric Anhydrosulphate*,  $\text{B}^2\text{H}^2\text{S}^2\text{O}^{12} = 2\text{H}(\text{BO})^2\text{SO}^4 \cdot \text{SO}^4$ , is formed by dissolving boric acid in strong sulphuric acid, and adding sulphuric anhydride, or by dissolving boric acid in fuming sulphuric acid. It separates, after some time, in leaf-like crystals, which melt and give off sulphuric anhydride when heated (Schultz-Sellack, *Deut. Chem. Ges. Ber.* iv. 12).

**BRAIN.** The composition of the grey and white matter of the brain has been examined by D. Petrovsky (*Pflüger's Archiv. f. Phys.* vii. 367). The grey layer was separated from the white by water, and a portion of the white matter was taken from the interior. Each substance was rubbed up rapidly in a mortar, and three extracts and a residue were obtained by digestion in cold alcohol, ether, and hot alcohol. The cold alcoholic extract contained a substance soluble, and another insoluble in anhydrous ether; the ether extract, lecithine, cholesterin, and fats; the warm alcoholic extract, lecithine and cerebrin; the residue, albuminous substances and salts. The portion of the cold alcoholic extract insoluble in ether does not contain sugar.

The dried grey substance consists about half of albumin and a quarter of cholesterin and fats, with very little cerebrin, its principal constituents therefore being albumin and water. In the white matter, on the contrary, cholesterin and fats form much more than half the dried mass, albumin a quarter of the whole substance, and cerebrin is present in considerable quantity.

**BRAZILIN**,  $\text{C}^{22}\text{H}^{10}\text{O}^7$  (E. Kopp, *Deut. Chem. Ges. Ber.* vi. 446).—This colourless



matter may be advantageously prepared from the dark brown-red crusts consisting of brazilin and a lime-brazilin lake, together with mechanical impurities and a resinous substance, which are deposited in considerable quantity during the preparation and storage of commercial extract of Brazil wood.

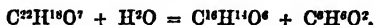
These crusts are saturated with water containing 5 p. c. of hydrochloric acid, and the washed residue is boiled with water containing 10 to 15 p. c. alcohol. The filtrate on cooling deposits the brazilin in beautiful yellowish crystals, which are easily purified by crystallisation from hot water. The crusts may also be boiled directly with water acidulated with hydrochloric or sulphuric acid, and the brazilin, which separates from the filtrate on cooling, purified by recrystallisation. The wash-waters and mother-liquors evaporated to dryness, with addition of a little chalk, leave a residue which yields resorcin by dry distillation.

Pure brazilin is colourless and gives with de-aerated water, colourless solutions which impart but faint colours to mordanted cotton. By contact with the air these solutions acquire a yellow and afterwards a reddish-yellow colour and an increased tinctorial power; at the same time, however, they become less and less capable of yielding crystallised brazilin.\*

Pure brazilin dissolves in dilute soda-ley with splendid carmine colour; and on heating this solution in the water-bath in a well-closed vessel with zinc-dust, reduction takes place, in consequence of which the liquid again becomes colourless. This colourless solution affords one of the most delicate tests for oxygen, the slightest access of air causing it to assume a deep carmine colour.

Brazilin (or the crusts from extract of Brazil wood, subjected to dry distillation in an iron or copper retort, yields, together with a large quantity of tumefied charcoal, a slightly coloured distillate, which, when passed through a wet filter (to separate tarry products), and concentrated on the water-bath, deposits on cooling, well-defined crystals of resorcin; this, indeed, is the simplest and easiest method of obtaining resorcin.

Brazilin is related to hæmatoxylin and resorcin in the manner shown by the following equation:—



#### BROMACETOPHENONE. See ACETOPHENONE.

**BROMAL**,  $\text{C}^2\text{HBr}^3\text{O} = \text{CBr}^3 - \text{CHO}$ .—This compound, discovered by Löwig (1st Suppl. 666), has been further examined by L. Schäffer (*Deut. Chem. Ges. Ber.* iv. 366). His mode of preparation is the same as that of Löwig, excepting that he uses the bromine in the state of vapour and in relatively smaller quantity. The bromal is found in the portion of the product which passes over on distillation between  $165^\circ$  and  $180^\circ$ , and is separated as a hydrate by mixing this liquid with water and repeatedly crystallising. The hydrate,  $\text{C}^2\text{HBr}^3\text{O} \cdot \text{H}^2\text{O}$ , melts at  $53.5^\circ$  and breaks up on distillation into water and anhydrous bromal, which boils at  $172^\circ - 173^\circ$ , and remains liquid at  $-20^\circ$ . Bromal unites with absolute alcohol, forming the *alcoholate*  $\text{C}^2\text{HBr}^3\text{O} \cdot \text{C}^2\text{H}^5\text{O}$ , which crystallises in thick needles, melts at  $44^\circ$ , and is decomposed by distillation into alcohol and bromal. Bromal treated with fuming nitric acid yields tribromacetic acid  $\text{CBr}^3 \cdot \text{COOH}$ .

The other products of the action of bromine on absolute alcohol are bromoform, carbon tetrabromide, dibromacetic acid, ethyl acetate, ethyl bromide and hydrogen bromide.

#### BROMHYDRINS. (L. Henry, *Ann. Ch. Pharm.* cliv. 363.)

**Tribromhydrin**  $\text{C}^3\text{H}^3\text{Br}^3$ .—This compound, obtained from glycerin, does not exhibit the properties hitherto ascribed to it on the authority of Berthelot a. De Luca (1st Suppl. 668), but rather agrees, both chemically and physically, with the tribromide of allyl which Wurtz obtained by the action of bromine on allyl iodide.

To obtain it in the pure state, Henry treated 1,600 grams of glycerin with 1,600 grams of phosphorus tribromide, obtaining thereby 800 grams of crude dibromhydrin, which was purified by systematic fractionation (80 grams of allyl bromide boiling at  $70^\circ$  are obtained as secondary product). The dibromhydrin was converted into tribromhydrin by treatment with phosphorus pentabromide; the phosphorus oxybromide and hydrobromic acid formed in the reaction were removed by successive washing with water and sodium carbonate; and the tribromhydrin which remained in the form of a heavy oil was dried with calcium chloride and then distilled. It passed over, with continuous evolution of hydrobromic acid,† almost wholly between  $200^\circ$  and  $221^\circ$ , the

\* These results are quite in accordance with those published some years ago by Preisser (l. 656), which have hitherto been treated as unworthy of credit.

† The hydrobromic acid probably originated, according to Henry, from glyceric bromophosphine formed by the action of the phosphorus oxybromide on the dibromhydrin, at all events not from the

principal portion between  $219^{\circ}$  and  $221^{\circ}$ . In a subsequent communication (*Deut. Chem. Ges. Ber.* iii. 601) Henry states that as tribromhydrin is very apt to retain water, and on account of its great density, which exceeds that of calcium chloride, is by no means easy to dry, it is best purified, not by simple rectification, but by crystallising it, removing the still liquid portion, and rectifying the crystals apart.

Pure tribromhydrin is undistinguishable from tribromide of allyl. It forms a colourless faintly ethereal liquid, insoluble in water, having a specific gravity of 2.407 at  $10^{\circ}$ , and solidifying in the cold to slender prismatic crystals, which melt at  $16^{\circ}$  to  $17^{\circ}$ . The solidifying point of the perfectly fused substance is perhaps much lower.

Heated in an oil-bath under ordinary pressure with potassium hydrate (in lumps) it behaves exactly like allyl tribromide, a brisk reaction setting in at  $140^{\circ}$ – $180^{\circ}$ , and a heavy oily liquid distilling over (together with a watery liquid), which in boiling point and amount of bromine, is intermediate between epibromhydrin  $C^3H^3BrO$  (b. p.  $138^{\circ}$ – $140^{\circ}$ ), and epibromhydrin  $C^3H^3Br^2$  (b. p.  $150^{\circ}$ – $152^{\circ}$ ). The liquid boiling at  $180^{\circ}$  described by Berthelot a. De Luca as tribromhydrin is, according to Henry, not properly designated by this name, and the body boiling at  $210^{\circ}$ , which they obtained as a bye-product in the preparation, and to which they assigned the formula  $C^3H^3Br^2 + H^2O$  or  $C^3H^3.OH.Br^2 + 2HBr$ , was impure tribromhydrin.

Berthelot (*Compt. rend.* lxx. 681) attributes the failure of Henry to obtain the true tribromhydrin (the existence of which as an individual compound distinct from allyl tribromide was demonstrated by himself and De Luca), and likewise the oxygenated addition-product, to the circumstance that Henry's experiments were performed under conditions different from those of Berthelot a. De Luca's. To meet this objection Henry (*Deut. Chem. Ges. Ber.* iii. 601) prepared tribromhydrin precisely according to the method described by Berthelot and De Luca, and obtained a product identical with the former. A similar result was obtained by the action of phosphorus pentabromide on epibromhydrin.

**BROMINE.** For the recovery of bromine from the residues of chemical operations containing alkaline bromides, Bolas a. Groves recommend distillation with potassium dichromate and dilute sulphuric acid. The solution of the alkaline bromide is introduced into a retort with the requisite quantity of the acid chromate in crystals, and an excess of sulphuric acid, previously diluted with half its weight of water, is gradually added; heat may be applied after the first powerful reaction is over. By this method, nearly the whole of the bromine is easily recovered, and there is no danger of breaking the retort (*Chem. Soc. J.* [2] ix. 784).

To obtain bromine perfectly free from chlorine and iodine, Adrian (*J. Pharm.* [4] xi. 20) washes it with water and small quantities of ether, which dissolves chloride of bromine, then digests it with a small portion of starch-paste to remove the iodine, and finally distils it.

The solidifying point of bromine has been variously given as  $-7^{\circ}$ ,  $-7.3^{\circ}$ ,  $-18^{\circ}$ ,  $-22^{\circ}$  and  $-25^{\circ}$ . According to H. Baumhauer (*Deut. Chem. Ges. Ber.* iv. 927) it is  $-24.5^{\circ}$ . Solidified bromine is a red-brown crystalline mass. The presence of water raises the solidifying point, owing to the formation of the hydrate.

**Action of Heat.**—When a narrow tube is half filled with liquid bromine, half with bromine-vapour, and after being sealed, is gradually heated till the temperature is raised above the critical point at which the liquid and gaseous states merge into one another (*1st Suppl.* 402) the whole of the bromine becomes quite opaque, and the tube has the aspect of being filled with a dark red opaque resin. A measure of the change in the power of transmitting light in this case may be obtained by varying the proportion of liquid and vapour in the tube. Even liquid bromine transmits much less light when strongly heated in a sealed tube than in its ordinary state (Andrews, *Chem. News*, iv. 75).

**Detection of Bromine.**—The following method of detecting bromine, chlorine, and iodine in organic substances, is founded on that of Berzelius for the detection of these elements in minerals, by means of cupric oxide and microcosmic salt. Some pure cupric oxide is placed on a loop of platinum-wire and heated for a short time to cause the oxide to adhere to the wire. If some of the suspected substance be now added and the loop again heated in the lower and inner edge of the flame of a gas-burner, the flame will assume a characteristic green or blue colour if either of the haloids be present. This reaction is applicable to all organic compounds (Beilstein *Deut. Chem. Ges. Ber.* v. 620).

**Detection of Bromine in Urine.**—The colour imparted by bromine, as well as by iodine, to chloroform or to carbon sulphide, is destroyed by agitation with urine, and tribromhydrin: for when the distillate, after removal of the dissolved hydrobromic acid by sodium carbonate and of the water by calcium chloride, was again rectified, the greater portion passed over at  $219^{\circ}$ – $221^{\circ}$  without decomposition.

this decolorising action has been attributed partly to uric acid and its salts, partly to the colouring matters of the urine, the iodine or bromine being supposed to fix itself on these constituents. There is, however, a difference in the behaviour of the two haloid elements under these circumstances, iodine when thus fixed being liberated with comparative facility by chlorine or by bromine, whereas the liberation of bromine by means of chlorine is more difficult. When equal quantities of potassium bromide are dissolved in equal volumes of distilled water and of urine, and the two solutions, after addition of carbon sulphide, are treated with chlorine-water, the former acquires a splendid red colour on addition of a single drop of the reagent, whereas the latter (the one containing the urine) requires a considerable quantity of chlorine-water before it exhibits any colour at all, and even then the tint is not red but only sulphur-yellow.

This difference appears to be due to the action of urea. This substance does not interfere with the liberation of iodine from its compounds by chlorine-water. Two test-tubes containing equal quantities of potassium iodide dissolved in equal volumes of water, the one pure, the other containing urea, exhibit exactly the same depth of violet colour when chloroform and a few drops of chlorine-water are added to each of them. But when a similar experiment is made with bromide of potassium, the result is very different, the chloroform in the tube containing the pure aqueous solution of the bromide acquiring a splendid orange-red colour on addition of chlorine-water, whereas that in the tube containing the solution to which urea has been added, acquires only a yellow colour. It is probable that urine contains also other substances capable of exerting this peculiar action on bromine, which appears to be different from that which is exerted by uric acid and the urinary pigments (Bizio, *Gazzetta chimica italiana*, ii. 339).

To detect alkaline bromides in urine, Cuigniet (*J. Pharm.* [4] x. 29) evaporates the liquid to dryness over the open fire, and ignites the residue gently for some time till the greater part of the organic matter is destroyed, and an aqueous extract of the residue appears quite colourless. The bromine may then be liberated with chlorine-water and recognised by the colour which it imparts to ether or to carbon sulphide. The quantitative estimation is made with a titrated solution of sodium hypochlorite. The aqueous extract is acidulated with citric acid, which does not act on the alkaline bromides, but liberates chlorine from the hypochlorite, and the bromine set free by this chlorine is taken up by repeated addition of carbon sulphide. As the liquid is thereby kept constantly colourless, it is easy to recognise the moment when an additional drop of the hypochlorite solution no longer imparts a perceptible colour to the carbon sulphide.

On the use of Bromine instead of Chlorine in Chemical Analysis, see ANALYSIS p. 70.

On the Volumetric Estimation of Bromine, see ANALYSIS, VOLUMETRIC, p. 71.

On the Estimation of Bromine in Platinum Compounds, see PLATINUM.

**Hydrogen Bromide or Hydrobromic acid.** Champion & Pellet (*Compt. rend.* lxx. 620) prepare this acid by the action of bromine on paraffin. The apparatus used consists of two tubulated retorts, one containing bromine, and the other paraffin, (melting at  $55^{\circ}$ ), the first being heated to about  $65^{\circ}$ , the second to  $185^{\circ}$  by means of an oil-bath or sand-bath. The retorts are connected by a tube which leads the bromine-vapour below the surface of the paraffin. A U-tube filled with phosphorus and wet fragments of glass serves to free the evolved hydrobromic acid from bromine mechanically carried over. The bromine acts on the paraffin, forming hydrobromic acid and substitution-products. After a certain time the passage of the bromine may be discontinued, because the brominated paraffin thus formed decomposes at about  $180^{\circ}$ , giving off nearly all the bromine that it has taken up, in the form of hydrobromic acid. Aqueous hydrobromic acid saturated at  $0^{\circ}$  by this process has a specific gravity of 1.78, and a composition agreeing with the formula  $\text{HBr} \cdot \text{H}_2\text{O}$ . When heated, it gives off part of its hydrobromic acid, leaving the hydrate  $\text{HBr} \cdot 5\text{H}_2\text{O}$ , which has a specific gravity of 1.48, and boils at  $126^{\circ}$ .

The following modification of the ordinary mode of preparation by the action of water on phosphorus bromide is given by Topsøe (*Zeitschr. f. Chem.* vi. 635). The materials used are 1 part of amorphous phosphorus, 10 parts of bromine, and 15 parts of water, a convenient portion of the water being put into the bulb-receiver, and the bromine added by drops. On distilling the product, the aqueous acid is obtained as a colourless liquid, the density and strength of which continually increase till the boiling point rises to  $125^{\circ}$ – $126^{\circ}$ , at which the maximum strength is attained. When the temperature rises still higher towards the end of the distillation, the acid which passes over becomes weaker, an effect which appears to be due to the fact that, at this high temperature, the residual phosphoric acid gradually gives up a portion of its water. The strongest hydrobromic acid obtained in the distillation has a specific gravity of 1.490, contains 48.17 p. c.  $\text{HBr}$ , and boils at  $125^{\circ}$ – $126^{\circ}$  (under a baro-

metric pressure of 758 mm.; at 124° under 747 mm.) It fumes rather strongly in the air, and may be kept for a long time without decomposition.

The same method may be applied to the preparation of a still stronger acid, if the quantity of water to be acted upon by the bromine and phosphorus in the flask, be reduced to a fifth of the weight of the bromine. The gaseous hydrogen bromide, which after a while is given off with great regularity, is then passed into water, or into an aqueous acid prepared as above.

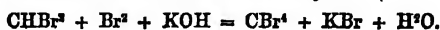
The following Table exhibits the density of hydrobromic acid of various strengths, as determined by Topsoë (*loc. cit.*):—

Temperature	Specific gravity	Percentage	Equivalent
°			
14	1·490	48·17	168·2
14	1·485	47·87	169·2
13	1·460	46·09	175·7
14	1·451	45·15	178·2
13	1·438	44·62	181·5
13	1·431	43·99	184·1
12	1·419	43·12	187·8
13	1·368	39·13	207·0
13	1·340	37·86	213·9
13	1·335	36·67	220·9
13	1·302	33·84	239·4
13	1·253	29·68	272·9
13	1·232	27·62	293·3
13	1·200	24·35	332·6
14	1·161	20·65	392·3
14	1·131	16·92	478·7
14	1·118	15·37	527·0
14	1·097	12·96	625·0
14	1·089	11·94	678·4
14	1·075	10·19	494·9
14	1·055	7·67	1056·1

All the values given in this table were determined directly, the percentages of acid by titration with soda. The specific gravities are referred to water at the same temperature, as unity.

The last column, headed 'Equivalent,' gives the quantities of the several aqueous acids containing 1 molecule of HBr = 81.

**BROMOFORM.** The conversion of this compound into carbon tetrabromide (1st Suppl. 400) takes place readily when a mixture of bromoform, bromine, and dilute potash is exposed to direct sunshine for five or six days:—



If no potash is present, the reaction goes on much more slowly (Habermann, *Deut. Chem. Ges. Ber.* vi. 174).

**BROMOPICRIN, CBr<sup>o</sup>NO<sup>i</sup>.**—(Bolas & Groves, *Chem. Soc. J.* [2] viii. 163, 775). This compound, which Stenhouse obtained by distilling picric acid with solution of calcium hypobromite (i. 923), may be conveniently prepared as follows: 4 parts of lime slaked with 50 parts of water are introduced into a glass flask, and after complete cooling, 6 parts of bromine are gradually added, care being taken to avoid rise of temperature; 1 part of picric acid is then added, and the mixture quickly distilled from a retort. The first fourth of the distillate contains the whole of the bromopicrin, which may be separated by water and dried over calcium chloride. The quantity thus obtained amounts to 46·5–49·5 p.c. of the bromine employed.

Bromopicrin is liquid at ordinary temperatures, but when quite pure, solidifies at low temperatures to a mass of prismatic crystals which melt at 10·25°. If the bromine used in the preparation contained chlorine, the melting point of the bromopicrin is lower. Its sp. gr. is 2·811 at 12·5° and its index of refraction for the line D at 20° is 1·57. It mixes in all proportions with benzene, carbon bisulphide, carbon tetrachloride, chloroform, light petroleum oil, and alcohol: from the alcoholic solution it is precipitated by water. It dissolves iodine, forming a violet liquid, also indigo in small quantity, and naphthalene with great facility. When treated with powerful brominating agents, it is partly converted into carbon tetrabromide (1st Suppl. 400).

Bromopierin, as observed by Stanhouse, decomposes rapidly when heated a little above  $100^{\circ}$ , and with explosive violence when a small quantity is quickly evaporated down, so that the side of the vessel becomes very hot; but when a considerable quantity is slowly heated, it decomposes quietly, yielding carbon tetrabromide (about 30 p.c. of the bromopierin) and a dark brown pungent liquid, which boils at  $56.5^{\circ}$  and has nearly the composition  $\text{NOBr}^4$  (bromine by analysis 92.84 p.c.; by calculation 91.42). Under reduced pressure, bromopierin may be distilled without decomposition. Heated with aqueous potassium cyanide it is entirely decomposed, cyanogen bromide being at first formed, but on further heating this compound is destroyed, and a dark brown compound remains in solution.

**BROMOXAFORM.**  $\text{C}^3\text{HBr}^3\text{O}^2$ . *Pentabromomethyl acetate*. (Lagermarch, *Zeitschr. f. Chem.* [2] vi. 299.) This body, which Cahours obtained by the action of bromine on potassium citrate, and on dibromocitraconic acid (1st Suppl. 370), is likewise produced by the action of bromine on pyrotartaric acid:



A mixture of 10 parts pyrotartaric acid (purified by once recrystallising from water and pressing) 24 pts. bromine, and 10 c.c. water is heated to  $120^{\circ}$  as long as brown fumes continue to escape, but no longer; otherwise further decomposition will take place, attended with separation of carbon. The contents of the tube, after cooling, consist of a pale yellow liquid and usually a white crystalline mass: on opening it, carbon dioxide escapes. The crystals are washed with a little water on a funnel having its neck stopped with fragments of glass, and the filtrate is mixed with 4 or 5 times its volume of water, and left to itself.

Bromoxaform thus purified melts at  $74.5^{\circ}$ . It is insoluble in water, easily soluble in alcohol and ether, and crystallises from the latter in white, silky needles, from alcohol in long four-sided prisms. The solutions are neutral. The ethereal solution decomposes in direct sunshine, with separation of bromine and a yellow unctuous mass. Bromoxaform dissolves in cold potash-ley, but is decomposed when heated therewith, yielding bromoform and oxalic acid:



**BRUCINE.** On the decomposition of brucine-salts by the electric current, see ALKALOIDS (p. 42).

*Brucine as a Test for Nitric Acid.*—It has already been noticed (1st Suppl. 370) that brucine treated with a chlorate or with chlorine tetroxide in presence of strong sulphuric acid, assumes an orange-red colour like that produced with nitric acid, but distinguished from the latter by not turning violet on addition of stannous chloride. According to Schün (Zeitschr. anal. Chem. 1870, 209) a solution of brucine in strong sulphuric acid is coloured rose-red and subsequently yellow by chlorine-water, hydrogen dioxide, potassium chlorate, sodium hypochlorite, chromic acid, potassium chromate, potassium ferricyanide and platonic chloride. Cupric chloride, gold chloride and ferric chloride produce the same effect under certain circumstances. It appears then that the production of a yellow or orange colour with brucine cannot be regarded as a trustworthy indication of the presence of nitric acid unless this colour is changed to violet on addition of stannous chloride.

According to S. Cotton (*J. Pharm.* [4] x. 18), solutions of brucine in nitric acid heated to  $40^{\circ}$ – $50^{\circ}$  and mixed with a strong solution of sodium sulphhydrate, assume first a violet, and then, on addition of an excess of the reagent, a green colour, the colour however disappearing after a day, with formation of a greenish precipitate. Alkalies do not alter the colour; dilute acids eliminate hydrogen sulphide, and change the colour to rose-red; 0.002 gram of brucine suffices to colour distinctly half a litre of water in this manner. As morphine does not exhibit any similar reaction, these two colour-reactions, the first of which is likewise produced by alkaline sulphates and thiosulphates, and by stannous chloride, may serve for the distinction of the two bases.

*Periodides of Brucine.*—Some of these compounds, prepared by Jørgensen, have already been described (1st Suppl. 371). The same chemist has also obtained the following penta-iodides:



These compounds form crystals having an almost metallic lustre, and behave towards reagents very much like the tri-iodides.

In crystallising the penta-iodide of ethylbrucine from hot alcohol, a small quantity of iodine is lost by each crystallisation. After eight or ten crystallisations, the tri-iodide comes down with the penta-iodide. Crystallisation of the penta-iodide from a strong solution of iodine causes it to take up an excess of iodine. By adding potassium iodide to a solution of brucine in hydrochloric acid, and leaving the mixture to slow oxidation, reddish-yellow needles were obtained, having the composition of a di-iodide of brucine,  $C^{23}H^{12}N^2O \cdot HI^2$ . This compound is probably a double salt of hydriodide and hydro-triiodide of brucine: for on cooling its alcoholic solution crystals of the tri-iodide were deposited, and the filtrate contained hydriodide of brucine.

A substance having the composition of a hexiiodide of amylbrucine,  $C^{23}H^{12}N^2O \cdot C^6H^{11}I^6$ , was obtained by adding to an alcoholic solution of the tri-iodide the calculated quantity of iodine. It appears in the form of bluish-green needles. It is difficultly soluble, even in boiling alcohol, and the solution deposits the tri-iodide on cooling (*J. pr. Chem.* [2] iii. 145).

**BUCKWHEAT.** *Polygonum sagopyrum*.—The composition of buckwheat grain from various localities has been determined by H. Weiske-Proskau (*Wochenblatt der Annalen du Landwirthschaft*, Sept. 6, 1871) with the following results:—

	Ordinary	Scotch	Tartarian
Water . . . . .	9.57	10.57	10.62
Albuminoids . . . . .	10.75	10.69	11.19
Soluble Carbohydrates } and Fat . . . . .	61.39	61.10	53.58
Crude fibre . . . . .	15.55	14.96	20.01
Ash . . . . .	2.74	2.68	4.60

**BUTYL ALCOHOLS and ETHERS.**—1. *Normal Butyl Alcohol*,  $CH^3CH^2CH^2CH^2OH$ . The preparation of this alcohol from butyric acid by converting the acid into a calcium salt, distilling this salt with an equivalent quantity of calcium formate, and reducing the resulting butyric aldehyde with sodium-amalgam (1st Suppl. 372), has been described in detail by Lieben & Rossi (*Ann. Ch. Pharm.* clviii. 137; *Chem. Soc. J.* [2] ix. 516). To obtain pure butyric acid for the purpose, the acid obtained by fermentation was freed as far as possible from acids of higher boiling point by fractional distillation, and the portion boiling between  $155^\circ$  and  $165^\circ$  (or better between  $159^\circ$  and  $164^\circ$ ) was dissolved in water, separated from the insoluble oil consisting of the higher acids, and converted into a calcium salt, which separated as a crust on the surface and could be skimmed off. The concentration and removal of the salt may be carried on for a longer or shorter time, according to the purity of the butyric acid used; generally speaking, however, the last mother-liquors do not yield a pure product. Butyric acid thus obtained boils at  $163.2$  under a pressure of 748.7 mm.

To prepare butyric aldehyde, the purified calcium butyrate, after being well pressed and dried, was intimately mixed with an equal weight of calcium formate, and the mixture was dried at about  $100^\circ$ , and then distilled in portions of about 10 grams from small retorts, the sides and bottoms of which were heated with charcoal. A brownish distillate was thus obtained, generally containing a little water, and on fractionally distilling it, the boiling point rose from  $50^\circ$  to  $200^\circ$ , but by repeated fractionation a portion boiled between  $70^\circ$  and  $80^\circ$  was obtained which was nearly pure butyric aldehyde. It amounted to about half the crude product, the other half consisting partly of aldehydes of lower boiling point, but chiefly of substances boiling above  $130^\circ$ , and not consisting of aldehydes. Alkaline bisulphites are not adapted for the purification of butyric aldehyde; they are of course useless for the separation of the lower aldehydes, and the bodies of higher boiling point can be more easily separated by fractional distillation. Normal butyric aldehyde obtained as above boils at about  $75^\circ$ ; it has the characteristic, pungent, slightly cough-provoking smell of aldehydes in general, dissolves in about 27 parts of warm water, and reduces silver oxide.

To convert the aldehyde into butyl alcohol 10 grams of it were mixed with 800 grams of water, that is, nearly but not quite enough to effect its solution. This mixture was treated successively with seven portions of 100 grams of 1 p.c. sodium-amalgam (theory requires 8.4 grams of sodium), the equivalent quantity of sulphuric acid being added at the same time as the sodium-amalgam, so as to keep the liquid always somewhat acid. When the action was ended, the liquid was distilled and the distillate

again treated with 300–400 grams of sodium-amalgam, together with the same quantity of sulphuric acid as above. The liquid was again distilled, and the products of the several operations purified together.

A small quantity of insoluble oil, which always forms during the operation, may be removed by filtration through wet filter-paper, and the butyl alcohol separated from the filtrate by a series of distillations. The butyl alcohol passes over with the first portions of the water. 100 grams of butyric aldehyde gave in different operations 80–90 grams of crude moist butyl alcohol. This product was dried as perfectly as possible with fused potassium carbonate; by far the largest quantity distilled between 110° and 120°, and it was easy to obtain the pure alcohol from the fraction which boiled between 113° and 117°. It is very difficult to remove the last traces of water from the butyl alcohol.\* This may, however, be effected by digestion, first with lime or baryta, and then by repeated distillation from sodium.

Normal butyl alcohol thus prepared gave in three combustions:

Carbon . . . . .	64.35	64.30	64.70	Calculated
Hydrogen . . . . .	13.41	13.53	13.33	64.86
				13.51

Its vapour-density was found by experiment to be 2.65, the calculated value being 2.56. Its specific gravity, as compared with that of water at the same temperature, is as follows:—

Temperature . . . . .	0°	20°	40°	99.1°
Specific gravity . . . . .	0.8242	0.8108	0.7998	0.7734

Another specimen of the alcohol obtained from the pure iodide by converting first into acetate and then into alcohol, gave

Temperature . . . . .	0°	20°	40°	98.9°
Specific gravity . . . . .	0.8230	0.8105	0.7994	0.7735.

This specimen of alcohol gave on combustion, carbon 64.72 p. c. of carbon.

The alcohol is not miscible with water, and like the aldehyde, requires a large excess of water to dissolve it. It dissolves in aqueous hydrochloric and hydrobromic acids. Sodium dissolves in it, forming an alcoholate which crystallises in a glistening mass of needles. This compound dried in the oil-bath yields a body which appears to have the composition  $\text{NaOC}_4\text{H}_9$  (Lieben and Rossi).

Linnemann (*Ann. Ch. Pharm.* clxi. 178–190) in preparing butyl alcohol from butyric aldehyde (obtained as above from butyric acid free from higher homologues), obtained a mixture of normal primary alcohol, with secondary and tertiary butyl alcohols, and methyl alcohol, as by treatment with gaseous hydriodic acid and fractional distillation of the product, it yielded methyl iodide, secondary and tertiary butyl iodide, and normal butyl iodide, boiling respectively at 41°–46°, 97°–99°, 115°–126°, and 127°–129°. The last-mentioned iodide, after repeated rectification, had the corrected boiling point 129.95° and sp. gr. 1.5909 at 16°. By converting this iodide into benzoate, purifying this ether by fractional distillation, saponifying it with potash, and dehydrating the volatile product with caustic baryta, normal butyl alcohol was obtained, having the corrected boiling point 116.88°. Another specimen obtained in like manner from a mixture of pure acetate, propionate and butyrate of butyl boiled at 116.96 (corr.). The alcohol from the benzoate was optically inactive, did not solidify at –22°, was soluble in 12 volumes of water at 22°, and dissolved 0.15 vol. water at the same temperature.

Linnemann has also prepared normal butyl alcohol by the action of sodium-amalgam on butyric anhydride or on a mixture of the anhydride with butyric acid, or of the acid with butyryl chloride, the last-mentioned method—which was also employed by

\* In a note by Lieben, to the paper above quoted, the different methods of drying alcohols are discussed. Melted potassium carbonate and anhydrous copper sulphate were not found capable of drying the alcohol. The sulphate remained unaltered in butyl alcohol containing 2 p.c. of water. Lime and baryta set better; but one treatment, even with a considerable quantity of lime, is seldom sufficient to effect the object. With respect to sodium, it has been frequently pointed out, especially by Chapman, that it does not confine its action to the water in the alcohol, but at the same time acts on the alcohol, and produces an alcoholate, and water will be found in the distillate, even though there be more than sufficient sodium present to combine with all the water. This observation is quite correct; but Chapman's conclusion that, therefore, sodium is not available for drying alcohols is not confirmed, as Lieben finds that the best method of drying alcohols is to distil them repeatedly from small quantities of sodium. He observes that it is necessary to heat the alcohol far above its boiling point in an oil-bath, to separate it from the alcoholate. To this Chapman replies (*Chem. Soc. J.* [2] ix. 518), that in the case of amyl alcohol, at all events, this method of drying is not available, as the hydrate of sodium, when distilled with a large excess of amyl alcohol, is completely decomposed into amylate and water. Common alcohol may be dried as above, but propyl and butyl alcohols from fermentation, not without great difficulty. On the other hand, caustic baryta dries these compounds perfectly.

Saytsoff (*J. pr. Chem.* iii, 76)—yielding the largest product. The distillate consists wholly or partly of butyl butyrate, which is decomposed by distillation with potash, and the butyl alcohol which then passes over is dehydrated with baryta. Linnemann purifies the butyl alcohol obtained by either of these methods, by converting it into iodide, submitting the latter to fractional distillation, converting the portion which boils at  $127^{\circ}$ – $130^{\circ}$  into benzoate, and decomposing the latter with potash as above.

**Normal Butylic Ethers.** The haloid ethers are prepared by the action of the corresponding haloid acids on the alcohol—*e.g.* the *chloride* by saturating the alcohol with hydrochloric acid gas; heating the resulting liquid with a small quantity of fuming hydrochloric acid to  $70^{\circ}$ , and finally to  $100^{\circ}$  in a sealed tube, till it separates into two layers which remain of constant volume, and purifying the upper layer, which consists of butyl chloride, by washing with strong hydrochloric acid, then with an alkali, and finally with water; then drying with calcium chloride, and rectifying. The *bromide* and *iodide* may also be prepared by treating the alcohol with bromine or iodine and amorphous phosphorus; the bromide also from the iodide, by decomposition with cupric bromide; and the chloride from the iodide by the action of mercuric chloride. The *acetate*, *propionate*, *butyrate*, and *benzoate* are obtained by decomposing the iodide with the corresponding silver salts. The following Table exhibits the boiling points and specific gravities of these ethers, as determined by Linnemann and by Lieben and Rossi:—

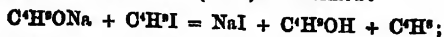
Normal Butyl Ethers.

	Boiling point	Specific gravity	Authority
Chloride	$77.6^{\circ}$ (bar. at 741.3 mm.)	0.9074 at $0^{\circ}$ 0.8874 „ $20^{\circ}$ 0.8972 „ $14^{\circ}$	Lieben a. Rossi — Linnemann
Bromide	$100.4^{\circ}$ (bar. at 744 mm.)	1.305 „ $0^{\circ}$ 1.2702 „ $20^{\circ}$ 1.2571 „ $40^{\circ}$ 1.2990 „ $20^{\circ}$	Lieben a. Rossi — — Linnemann
Iodide	$129.6^{\circ}$ (bar. at 738.2 mm.)	1.643 „ $0^{\circ}$ 1.6136 „ $20^{\circ}$ 1.5894 „ $40^{\circ}$ 1.5804 „ $18^{\circ}$	Lieben a. Rossi — — Linnemann
Cyanide	$129.65^{\circ}$	0.8164 „ $0^{\circ}$	Lieben a. Rossi
Acetate	$140.4^{\circ}$ (bar. at 739.3 mm.) $125.1^{\circ}$ ( „ „ 740)	0.900 „ $0^{\circ}$ 0.8817 „ $20^{\circ}$ 0.8659 „ $40^{\circ}$ 0.8768 „ $23^{\circ}$ 0.8828 „ $15^{\circ}$	— — — Linnemann
Propionate	$124.30^{\circ}$	0.8855 „ $0^{\circ}$	—
Butyrate	$146^{\circ}$ $165.5^{\circ}$ (bar. at 735.7 mm.)	0.8717 „ $20^{\circ}$ 0.8570 „ $40^{\circ}$ 0.8760 „ $12^{\circ}$	Lieben a. Rossi — Linnemann
Benzoate	$164.8^{\circ}$ $247.32^{\circ}$	1.000 „ $20^{\circ}$	—

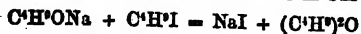
The chloride, butyrate and benzoate are insoluble in water; the acetate dissolves in 90 parts of water at  $20^{\circ}$  (Linnemann).

**Brominated Butyl Bromide**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ . Br obtained by heating 8 parts of the normal bromide with 9 of bromine to  $150^{\circ}$  for five hours boils at  $166^{\circ}$ – $167^{\circ}$ : hence it appears to be identical with Wurtz's dibromide of ethyl-vinyl, boiling at  $166^{\circ}$  (*1st Suppl.* 377) and isomeric with the dibromide of methyl-allyl, boiling at  $156^{\circ}$ – $159^{\circ}$ , (*ibid.* 376) from both of which again, the dibromide of isobutylene differs, its boiling point being  $149^{\circ}$  (Linnemann).

**Normal Butyl Iodide** is not much acted upon by sodium butylate in the cold, but on heating the materials in a flask, with inverted condenser, a small quantity of butylene is evolved, and butyl oxide  $(\text{C}_4\text{H}_9)_2\text{O}$  is formed:



also

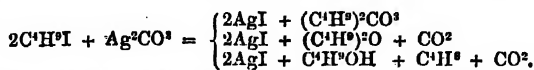


The normal butyl oxide thus obtained boiled, after repeated distillation over



sodium, at 140.5° (bar. at 741.5 mm. corrected and reduced to 0°). Sp. gr. = 0.784 at 0°, 0.7685 at 20°, 0.7556 at 40° (Lieben a. Rossi, *Ann. Ch. Pharm.* clxv. 109).

Butyl iodide heated in like manner with silver carbonate yields a product separable by fractional distillation into normal butyl carbonate, butyl alcohol, and butyl ether:



Normal butyl carbonate has a sp. gr. of 0.9407 at 0°, 0.924 at 20°, 0.911 at 40°, and boils at 207° (bar. 740 mm.); fermentation butyl carbonate, according to Wurtz, at 190° (Lieben a. Rossi).

The difference of boiling point between the oxide and carbonate of normal butyl, (which contain 2 atoms of butyl), and the corresponding isobutyl ethers, is about twice as great as that which exists between normal and isobutyl ethers, which contain only 1 atom of butyl, such as the chloride, acetate, cyanide, &c.

*Normal Butylsulphuric acid* is formed by gradually adding sulphuric acid to cooled butyl alcohol. On diluting with water, neutralising with baryta-water, crystallising, and drying over sulphuric acid, the *barium salt*,  $\text{Ba}(\text{C}^4\text{H}^9\text{SO}^4)^2 + \text{H}^2\text{O}$ , is obtained: it is stable at 60°, but decomposes at 100° (Lieben a. Rossi).

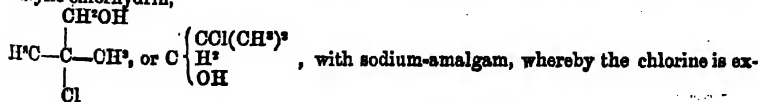
*Butyl-ethyl oxide or Butyl-ethyl ether*,  $\text{C}^4\text{H}^9\text{O} = \begin{smallmatrix} \text{C}^4\text{H}^9 \\ \text{C}^2\text{H}_5 \end{smallmatrix} \text{O}$ , is obtained, together with a small quantity of butylene, by heating butyl bromide or iodide with sodium ethylate or alcoholic potash, the quantity of butylene being larger with the latter reagent than with the former. When 10 grams of normal butyl iodide were warmed with a solution of 5 grams of potash in 15 grams of 90 p.c. alcohol, and 5 grams of solid potash, in a flask provided with a reversed condenser, only one-third of the butyl iodide was converted into butylene, the chief product, even with this large excess of potash, being butyl-ethyl ether. This ether boils at 91.7° under a pressure of 742.7 mm. Its specific gravity is 0.7694 at 0°, 0.7522 at 20°, and 0.7367 at 40° (Lieben a. Rossi).

**Isobutyl Alcohol.**— $\text{CH}(\text{CH}^3)_2.\text{CH}^2\text{OH}$ . This alcohol, separated by Linnemann's method of fractional distillation (see DISTILLATION) from the products of the alcoholic fermentation of corn or molasses, is optically inactive, boils at 108.39°, has a sp. gr. of 0.8003 at 18°, and dissolves in 15 parts of water at 15° (Linnemann, *Ann. Ch. Pharm.* cxl. 195).

It may be formed systematically from normal butyl alcohol by the following series of processes: 1. The normal alcohol is converted into normal butyric acid by oxidation with chromic acid. 2. The ammonium salt of this acid distilled with dry zinc chloride yields butyronitril,  $\text{C}^4\text{H}^7\text{N}$ . 3. The nitril treated with hydrochloric or sulphuric acid and zinc takes up 4 atoms of hydrogen, and is converted into normal butylamine  $\text{C}^4\text{H}^{11}\text{N}$ . 4. This base heated with silver nitrite and water (*1st Suppl.* 63) yields a butyl alcohol which boils between 105° and 110°, dissolves in 8 to 9 parts of water at 22°, is converted by oxidation into an acid having the composition  $\text{C}^4\text{H}^8\text{O}_2$ , and yields an iodide boiling between 119° and 121°: it is therefore identical with the butyric alcohol of fermentation (*1st Suppl.* 373) (Linnemann a. von Zotta, *Ann. Ch. Pharm.* clxii. 3).

2. From isobutyric acid, by distilling the calcium salt of that acid with calcium formate, and treating the isobutyric aldehyde  $\text{CH}(\text{CH}^3)_2.\text{CHO}$ , thereby obtained, with sodium-amalgam (Linnemann a. von Zotta, *ibid.* 7).

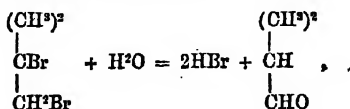
3. From tertiary butyl alcohol, or trimethyl carbinol, by converting this alcohol into the corresponding butylene or dimethyl-ethylene  $\text{H}^3\text{C}-\overset{\text{CH}^3}{\underset{\text{C}}{\text{C}}}-\text{CH}^3$ , combining this hydrocarbon with hypochlorous acid, and treating the resulting isobutylic chlorhydrin,



changed for hydrogen, and isobutyl alcohol  $\text{C} \begin{cases} \text{CH}(\text{CH}^3)^2 \\ \text{H}^2 \\ \text{OH} \end{cases}$  is produced (*1st Suppl.* 376).

The same result is attained by heating the dibromide of dimethyl-ethylene  $\text{CH}^3\text{Br}$   
 $\text{H}^3\text{C}-\text{C}-\text{CH}^3$  (which is identical with monobrominated trimethyl-carbinyl bromide,  
 $\text{Br}$

and with the dibromide of isobutylene, and may also be produced by acting on isobutyl-iodide with bromine not in excess) with 20 volumes of water to 150°-160° for 24 hours, whereby isobutyric aldehyde is formed:



which may be converted into the alcohol by sodium-amalgam (Linnemann a. von Zotta, *Ann. Ch. Pharm.* cxlii. 33).

**Isobutyl Bromide**,  $\text{CH}(\text{CH}^3)^2\text{CH}^2\text{Br}$ , prepared by treating the alcohol with phosphorus and bromine, and purified in the usual way by washing, drying and fractional distillation, is a colourless mobile liquid having a pleasant but slightly alliaceous odour, boiling at 90.5°, and having a specific gravity of 1.249 at 0°, 1.191 at 40.2° and 1.1408 at 73.5° (Pierre a. Puchot, *J. Pharm.* [4] xiii. 9).

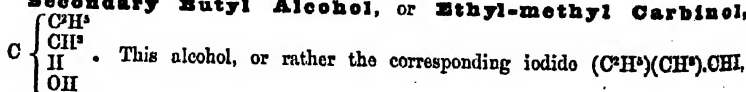
**Isobutyl Chloride**,  $\text{CH}(\text{CH}^3)^2\text{CH}^2\text{Cl}$  prepared by saturating the alcohol with hydrogen chloride, or treating it with phosphorus pentachloride, is a limpid liquid, having a pleasant, ethereal, but slightly alliaceous odour, and boiling at 60° under ordinary pressure. Sp. gr. = 0.8953 at 0°, 0.8651 at 27.8°, 0.8281 at 59°. Its specific volume at different temperatures is given in the following table, the volume at the boiling point being taken as unity:—

Distance in degrees Centigrade from the boiling point	Specific Volume
0	1.0000
10	0.9848
20	0.9705
30	0.9570
40	0.9443
50	0.9322
60	0.9208
70	0.9101

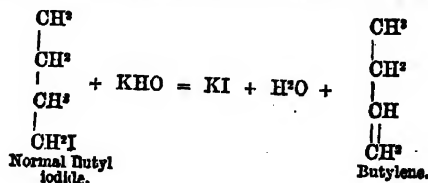
(Pierre a. Puchot, *Compt. rend.* lxxii. 832).

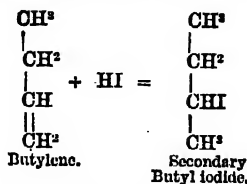
**Isobutyl Iodide**,  $\text{CH}(\text{CH}^3)^2\text{CH}^2\text{I}$ , boils at 120.63° (Linnemann), at 122.5° (Pierre a. Puchot). On heating it with water in a retort, the two liquids distil over together at a constant temperature of 95° or 96°, the distillate containing 70 parts butyl iodide to 21 parts water, whatever be the proportion of the two in the retort. During the distillation bubbles of vapour are seen to rise from the junction of the two layers of liquid, each bubble carrying with it a drop of iodide (Pierre a. Puchot, *Compt. rend.* lxxiv. 224).

### Secondary Butyl Alcohol, or Ethyl-methyl Carbinol,



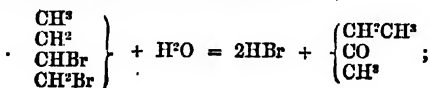
originally obtained by the action of hydriodic acid on erythrite, and afterwards by the successive action of zinc-ethyl and hydriodic acid on chlorinated ethyl oxide (*1st Suppl.* 373), may likewise be formed from normal butyl alcohol, by first converting that alcohol into the corresponding iodide  $\text{CH}^3\text{CH}^2\text{CH}^2\text{CH}^2\text{I}$ , heating this iodide with an alcoholic solution of potash, whereby butylene is produced, and combining this butylene with hydriodic acid, whereby secondary butyl iodide is obtained:





The iodide thus obtained, which distils almost wholly between  $116^{\circ}$  and  $120^{\circ}$ , is converted in the ordinary way into the corresponding acetate  $(\text{CH}^{\text{a}})(\text{C}^{\text{a}}\text{H}^{\text{a}}).\text{CH}(\text{OC}^{\text{a}}\text{H}^{\text{a}}\text{O})$ , (b.p.  $110^{\circ}$ – $113^{\circ}$ ), and this, by saponification, into secondary butyl alcohol, boiling between  $97^{\circ}$  and  $100^{\circ}$ . This alcohol yields by oxidation methyl-ethyl ketone and acetic acid (Saytzeff, *Zeitschr. f. Chem.* vi. 327).

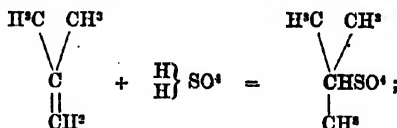
When normal brominated butyl bromide,  $\text{CH}^{\text{a}}-\text{CH}^{\text{a}}-\text{CHBr}-\text{CH}^{\text{a}}\text{Br}$  (identical with the dibromide of normal butylene) is heated with 20 times its volume of water to  $150^{\circ}$  for 24 hours, a ketone boiling between  $75^{\circ}$  and  $80^{\circ}$  is formed, which is doubtless ethyl-methyl ketone, produced by the reaction:



and this ketone by hydrogenation would doubtless yield ethyl-methyl carbinol (Linne-mann, *Ann. Ch. Pharm.* cxlii. 1).

#### Tertiary Butyl Alcohol, or Trimethyl Carbinol, $\text{C}(\text{CH}^{\text{a}})^3.\text{OH}$ .

—This alcohol, originally formed by the action of water on the product obtained by treating acetyl chloride with zinc-methyl (Butlerow), was afterwards obtained by combining isobutylene (from isobutyl iodide) with hydriodic acid, whereby tertiary butyl iodide or trimethyl-carbinyl iodide  $(\text{CH}^{\text{a}})^3.\text{CI}$  is produced, and decomposing this iodide with moist silver oxide (Markownikoff, see 1st Suppl. 374). Butlerow (*Zeitschr. f. Chem.* [2] vi. 237) modifies the process by passing the gaseous isobutylene into sulphuric acid, whereby trimethyl-carbinyl-sulphuric acid is formed:



and converting this acid into trimethyl carbinol by distillation with water. The details of the process are as follows:—

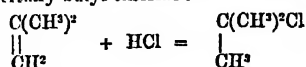
1. Isobutyl iodide is prepared by passing hydrogen iodide into boiling isobutyl alcohol in an apparatus provided with a condensing tube; at ordinary temperatures very little iodide is formed, but the alcohol saturated with hydrogen iodide at ordinary temperatures takes up a larger quantity when heated, and is then completely converted into isobutyl iodide. Butlerow recommends this process for preparing the iodides of the rarer alcohols.

2. To prepare isobutylene, 4 parts of alcoholic potash (1 part KHO to 3 parts alcohol of 90 p.c.) and  $\frac{1}{2}$  part pulverised potassium hydrate are introduced into a flask provided with a funnel and condensing tube, and 2 parts of isobutyl iodide are gradually poured in through the funnel. The mixture is gently heated to start the reaction, which then goes on of itself, but towards the end heat must be again applied, only, however, to the sides of the flask, to prevent fracture. If less than the preceding quantity of potash be used, the quantity of isobutylene obtained is small, probably in consequence of the formation of ethyl-isobutyl ether. The isobutylene gas, after washing with alcohol and then with water, is collected in a gas-holder. 100 grams of isobutyl iodide thus treated yielded 10 to 11 litres of isobutylene.

3. The absorption of the isobutylene by sulphuric acid is effected as follows:—Within an upright Liebig's condenser 0.5 to 0.6 met. long is fixed a tube 1 centimeter in diameter, filled with coarsely pounded glass, and closed at top and bottom with caoutchouc stoppers. Through the lower of these stoppers are inserted two delivery tubes, one, intended for the butylene, passing upwards to the height of a decimeter into the pounded glass, while the other, which serves as exit-tube for the sulphuric acid, reaches only to the upper surface of the stopper. This last tube is bent upwards

outside the condenser, to the length of 8 centimeters, and then backwards like a fork. This tube consequently always remains full of acid, and thus stops the passage of the gas. Into the upper stopper are fitted a gas-delivery tube and a funnel-tube, provided with a stop-cock, through which the sulphuric acid drops slowly on to the glass. The dried isobutylene is now slowly admitted from below, care being taken to provide good refrigeration during the whole of the experiment, since in the absorption of the gas by the acid (3 parts  $\text{H}_2\text{SO}_4$  to 1 part water) much heat is evolved which gives rise to the formation of an oily by-product. For the same reason the acid saturated with the isobutylene must be slowly dropped into cold water, and only a very dilute solution subjected to distillation. The watery distillate which contains the trimethyl carbinol is filtered to separate a trace of oil, then saturated with dry potassium carbonate to separate the alcohol. 85 litres of butylene yielded by this process 20 grams of dry trimethyl carbinol: consequently the 10 litres of isobutylene obtained as above from 100 grams of isobutyl iodide would yield 23.5 grams of trimethyl carbinol. Pure fermentation butyl alcohol should accordingly yield about half its weight of the tertiary alcohol.

Hydrochloric acid heated with isobutylene acts upon it in the same way as hydriodic acid, converting it into tertiary butyl chloride:



The action does not take place at ordinary temperatures; but when isobutylene is condensed by strong cooling in tubes containing very concentrated hydrochloric acid, and the tubes, after being sealed, are heated for several hours in a water-bath, the whole of the isobutylene is converted into the tertiary chloride, which floats as a layer on the top, no gas being evolved on opening the tube. The tertiary chloride, heated with water in a retort with reversed condenser, is converted into trimethyl carbinol (Salessky, *Ann. Ch. Pharm.* clxvi. 92).

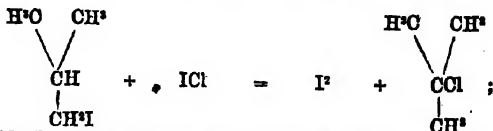
Other methods of passing from isobutyl alcohol to the tertiary alcohol have been devised by Linnemann (*Ann. Ch. Pharm.* clxii. 12).  $\alpha$ . A mixture of freshly precipitated silver oxide or mercuric oxide and glacial acetic acid acts on isobutyl iodide at ordinary temperatures, producing trimethyl-carbinyl acetate and trimethyl carbinol, together with isobutylene and a small quantity of a gas not absorbed by bromine. From the isobutylene thus formed, a further quantity of trimethyl carbinol may be obtained by Butlerow's process above described. This method of preparing trimethyl carbinol and its derivatives appears indeed to be the most productive known, inasmuch as 100 parts of isobutyl iodide thus treated yield directly 27.5 parts of trimethyl carbinol and 11 parts of isobutylene, which when treated by Butlerow's method yield an additional 11 parts of trimethyl carbinol, in all therefore 38 parts of the tertiary alcohol, the theoretical yield being 40, whereas Butlerow's process directly applied to 100 grams of isobutyl iodide yielded, as above stated, only 23.5 grams of trimethyl carbinol.

The formation of trimethyl carbinol from isobutyl iodide by means of silver oxide and glacial acetic acid may be explained by supposing that the elements of hydriodic acid are first removed, forming isobutylene, which, in the nascent state, combines with the elements of the acetic acid forming trimethyl-carbinyl acetate. The simultaneous formation of this acid, trimethyl carbinol, and isobutylene is in favour of this view.

According to Butlerow (*Ann. Ch. Pharm.* clxviii. 143), the butyl alcohol obtained by this process is a mixture of about equal parts of trimethyl carbinol and isobutyl carbinol, so that the advantage obtained by it is not so great as stated by Linnemann. Butlerow also finds that the quantity of silver oxide used by Linnemann, viz., that obtained from 50 parts of silver nitrate to 30 grams of the isobutyl iodide, which is about twice the calculated quantity, affords no advantage, the oxide from 30 grams of silver nitrate being quite sufficient for the same quantity of iodide.

$\beta$ . Isobutyl bromide treated with mercuric oxide and glacial acetic acid likewise yields trimethyl carbinol; but silver oxide does not act upon it. Isobutyl chloride is scarcely acted upon by either of these oxides mixed with glacial acetic acid.

$\gamma$ . Iodine monochloride converts isobutyl iodide into trimethyl-carbinyl chloride thus:



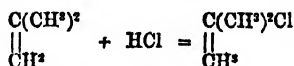
and this chloride (b.p.  $46^{\circ}$ – $52^{\circ}$ ) heated to  $100^{\circ}$  with water for several hours is almost wholly converted into trimethyl carbinol.

8. Isobutyl iodide heated with dry silver cyanate yields isobutyl cyanate; and this ether mixed with finely powdered potassium hydrate and heated in small quantities at a time, gives off vapours, not of isobutylamine, but of trimethyl-carbinylamine or tertiary butylamine,  $C(CH^3)_3.NH^2$ ; and the hydrochloride of this amine heated with silver nitrate and water yields trimethyl carbinol (Linnemann).

For the dehydration of trimethyl carbinol, Butlerow combines it with calcium chloride and decomposes the resulting compound by distillation. Linnemann prefers the use of caustic baryta, as he finds that the alcohol, in distillation from its compound with anhydrous calcium chloride, which requires a temperature of  $150^{\circ}$ – $200^{\circ}$ , is partly etherified; if the calcium chloride used contains so much water that the alcohol can be distilled off in the water-bath, the distillate contains as much water as the original alcohol before treatment with calcium chloride. By repeated treatment with caustic baryta in sealed tubes and subsequent fractional distillation, Linnemann obtained from the crude product, 74 p.c. of pure anhydrous trimethyl carbinol.

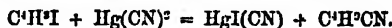
Trimethyl carbinol crystallises at temperatures below  $+20^{\circ}$  in large rhombic, doubly refracting prisms, which melt at  $25^{\circ}$ – $25.5^{\circ}$  and readily attract water, whereby they are liquefied (Butlerow, *Zeitschr. f. Chem.* [2] vii. 273). According to Linnemann, it melts at  $23^{\circ}$ – $24^{\circ}$  and often remains liquid at temperatures below the melting point, solidifying suddenly on agitation or on throwing into it a piece of thin platinum wire. It boils at  $82.94^{\circ}$  (Linnemann); at  $82.5^{\circ}$  under a pressure of 750 mm. (Butlerow). Sp. gr. = 0.7792 at  $37^{\circ}$  (Linnemann); 0.7788 at  $30^{\circ}$ ; its coefficient of expansion between  $30^{\circ}$  and  $50^{\circ}$  is 0.0136 for  $1^{\circ}$  (Butlerow). On adding water to anhydrous trimethyl carbinol, considerable contraction takes place. The hydrate  $2C(CH^3)_3.OH + H^2O$  is liquid at  $0^{\circ}$ , boils constantly at  $80^{\circ}$  and crystallises at the temperature of a mixture of snow and salt, in fine, silky needles (Butlerow).

*Tertiary Butyl Chloride*,  $C(CH^3)_3.Cl$ , is obtained by passing isobutylene into very strong hydrochloric acid in tubes cooled by a freezing mixture, then sealing the tubes, and heating them to  $100^{\circ}$  for several hours:



An oily liquid is thereby formed which is converted into trimethyl carbinol by boiling with water (Salessky, *Ann. Ch. Pharm.* clxv. 92).

*Tertiary Butyl Iodide*,  $C(CH^3)_3.I$ , heated with dry mercuric cyanide is converted into the corresponding cyanide, according to the equation:



The reaction is very violent, and must be moderated by cooling, but even then, a certain quantity of gaseous isobutylene is given off. The product distilled with water yields an oil containing the nitril,  $C^3H^7CN$ , together with a small quantity of isocyanide, which may be decomposed by hydrochloric acid. The portion of the oil boiling at  $90^{\circ}$ – $120^{\circ}$  consists chiefly of the nitril; the higher portions up to  $200^{\circ}$  which constitute the larger portion, consist mainly of polymeric isobutylenes. The nitril boils at about  $103^{\circ}$ . On decomposing it in a digester with alcoholic potash, extracting the potassium salt with alcohol, distilling it with sulphuric acid, and dehydrating the distillate with phosphoric anhydride, trimethyl-acetic acid,  $C(CH^3)_3.CO^2H$ , is obtained, which solidifies immediately to a vitreous mass interspersed with crystals, melts at  $31^{\circ}$ – $36^{\circ}$  and boils at  $181^{\circ}$  (Butlerow, *Deut. Chem. Ges. Ber.* v. 478).

**BUTYLAMINES.** (Lieben a. Rossi, *Ann. Ch. Pharm.* clviii. 172; Linnemann, *ibid.* clxii. 3). *Normal butylamine*,  $C^4H^9N = N \begin{Bmatrix} CH^3CH^2CH^2(CH^3) \\ H^2 \end{Bmatrix}$ , is prepared by heating butyl chloride to  $100^{\circ}$ – $110^{\circ}$  in sealed tubes for two days with solid potassium cyanate and alcohol, and digesting the resulting alcoholic liquid, which contains butyl cyanate, with caustic potash. On distilling the liquid to dryness, adding water and again distilling, acidulating the mixture of the two distillates with hydrochloric acid, again evaporating to dryness, and exhausting the residue with alcohol, a solution is obtained, containing the hydrochlorides of butylamine, dibutylamine and tributylamine, while sal-ammoniac remains undissolved. The alcoholic extract evaporated to dryness and distilled with lime from a combustion-tube, the front part of which contains anhydrous baryta, yields a mixture of the three normal butylamines, from which the monobutylamine is easily separated by fractional distillation; the di- and tri-butylamine are less easy to separate. The three butylamines are likewise obtained as by-products in the preparation of normal valeric acid from butyl cyanide (Lieben a. Rossi.)

Normal butylamine may also be prepared by hydrogenising butyronitril  $C^4H^7N$ , (boiling at  $115^{\circ}$ – $117^{\circ}$ ) which is obtained by distilling with zinc chloride the ammonium salt of normal butyric acid. By mixing this butyronitril with hydrochloric or sulphuric acid, and allowing the mixture to flow on to zinc, a small quantity of butylamine is formed, and an additional quantity may be obtained by distilling off the unaltered nitril and repeating the process from twenty to twenty-five times (Linnemann).

Normal butylamine is a colourless, hygroscopic, ammoniacal-smelling, fuming liquid, which boils at  $75.5^{\circ}$  under a pressure of 740 mm. and has a sp. gr. of 0.7553 at  $0^{\circ}$ , 0.7333 at  $20^{\circ}$  (Lieben a. Rossi); boils at  $76^{\circ}$ – $77^{\circ}$  and has a sp. gr. of 0.740 at  $20^{\circ}$  (Linnemann). Its vapour produces a feeling of heat on the skin, and strongly attacks cork and caoutchouc. It mixes in all proportions with water, and the solution precipitates the salts of lead, aluminium, magnesium, copper and silver. The copper and silver precipitates, and apparently also the aluminium precipitate, are soluble in excess of butylamine.

Hydrochloride of Butylamine is very soluble in alcohol, melts at  $195^{\circ}$ , decomposes to a great extent when distilled (Linnemann).

The platino-chloride,  $2(C^4H^9N.HCl).PtCl_4$ , crystallises in golden-yellow plates slightly soluble in cold, moderately soluble in hot water; soluble also in alcohol.

Normal butylamine is converted by nitrous acid, not into normal butyl alcohol, but into isobutyl alcohol (Linnemann); see p. 217.

Dibutylamine  $NH(C^4H^9)^2$ , boils at  $160^{\circ}$  and forms a platino-chloride, crystallising in long needles which melt and dissolve easily in hot water, very sparingly in cold water.

Tributylamine  $N(C^4H^9)^3$ , is prepared by heating with butyl iodide and alcohol, the mixture of primary, secondary, and tertiary amines obtained as a by-product in the synthesis of normal valeric acid from butyl cyanide. By boiling the product with caustic potash, tetrabutylammonium iodide and tributylamine are formed. The former is not attacked by boiling caustic potash, but is quickly decomposed by moist silver oxide. The latter boils between  $211^{\circ}$  and  $215^{\circ}$  (corr.) under a pressure of 740 mm. (tributylamine from fermentation butyl alcohol boils at about  $30^{\circ}$  lower); it forms a crystalline hydrochloride, from which caustic potash or ammonia precipitates the base as an oily liquid (Lieben a. Rossi, *Ann. Ch. Pharm.* clxv. 109). The platino-chloride  $2(C^4H^9N.HCl).PtCl_4$  crystallises in groups of small needles, which melt and are slightly soluble in warm water, very slightly soluble in cold water, more freely in alcohol (Linnemann).

Isobutylamine,  $N\begin{Bmatrix} CH^2CH(CH^3) \\ H^2 \end{Bmatrix}$ , discovered by Wurtz, and already described under the name of tetrylamine (v. 737) is obtained by distilling a mixture of the potassium salt of isobutylsulphuric acid and potassium cyanate, and treating the product with caustic potash. It boils at  $69^{\circ}$ – $70^{\circ}$  (Wurtz), at  $65.8^{\circ}$ – $68.3^{\circ}$  under a pressure of 743 mm. (Linnemann); has a sp. gr. of 0.7357 at  $15^{\circ}$ ; dissolves in all proportions of water, and solidifies on exposure to the air, forming a carbonate. Its hydrochloride dissolves in 0.73 pt. water at  $15^{\circ}$ , and melts at  $160^{\circ}$  (below  $100^{\circ}$  according to Wurtz). The platino-chloride is slightly soluble in water (Linnemann).

Hydrochloride of isobutylamine distilled with silver nitrite and water yields, not isobutyl alcohol, but tertiary butyl alcohol or trimethyl carbinol  $C(CH^3)_3.OH$ , boiling at  $81^{\circ}$ – $85^{\circ}$ ; and it has been already stated that normal butylamine similarly treated yields isobutyl alcohol; it is found also that normal propylamine gives isopropyl alcohol. The action of nitrous acid on monamines, may therefore be described as always producing the alcohol of a radicle containing one more methyl group than the original amine (provided of course that the amino is capable of forming an isomeride containing one more methyl group) (Linnemann).

Isobutylamines prepared by K. Reimer from isobutyl alcohol obtained by Krämer a. Pinner's process from the 'first runnings' of fused oil, are described by A. W. Hofmann (*Deut. Chem. Ges. Ber.* iii. 756). The alcohol boiled at  $108^{\circ}$ ; treated with bromine and phosphorus it yielded (besides butylene hydrobromide) isobutyl bromide boiling at  $87^{\circ}$ – $88^{\circ}$ . This bromide heated to  $150^{\circ}$  with alcoholic ammonia yielded a mixture of three isobutylamines, which were but imperfectly separable by fractional distillation, but were easily separated by the application of Hofmann's oxalic ether method to the suitable fractions, into mono-isobutylamine boiling at  $62^{\circ}$ – $65^{\circ}$  and di-isobutylamine boiling at  $120^{\circ}$ – $122^{\circ}$ . The highest boiling portion of the crude mixture of bases, when further treated with the isobutyl bromide, yielded the hydrobromide of a nearly pure tri-isobutylamine  $N(C^4H^9)^3$  boiling at  $177^{\circ}$ – $180^{\circ}$ . This base digested with the bromide yielded, not the tetrabutylammonium compound

The *sulpho-carbimide*, or *isoculpho-cyanate*,  $N\{C\overset{S}{\underset{H}{H}}\}$ , derived from mono-isobutylamine, boils at  $161^{\circ}$ – $168^{\circ}$ , and forms with ammonia a well-crystallised urea  $CS(NH^2)[NH(C^2H^5)]$  melting at  $90^{\circ}$ – $91^{\circ}$ . The isomeric *isobutyl sulpho-cyanate*  $S\{C\overset{CN}{\underset{H}{H}}\}$  produced by the action of potassium sulphocyanate on isobutyl sulphate boils at  $174^{\circ}$ – $176^{\circ}$ .

*Tertiary Butylamine* or *Trimethyl-carbinylamine*,  $N\{C(CH^3)_2\}$ , is prepared by heating isobutyl iodide with dry silver cyanate, mixing the resulting solid compound of silver iodide and isobutyl cyanate with finely pulverised potassium hydrate, and heating the mixture by small quantities at a time. Vapours of trimethyl-carbinylamine (not of isobutylamine) are then given off; these may be absorbed by hydrochloric acid, and the resulting hydrochloride of tri-carbinylamine separated from sal-ammoniac by digestion with alcohol after evaporation to dryness.

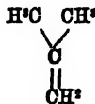
Pure trimethyl-carbinylamine separated from the hydrochloride by distillation with an alkali, is a liquid boiling at  $45^{\circ}$ – $46^{\circ}$  and having a sp. gr. of 0.6987 at  $16^{\circ}$ . Its hydrochloride melts above  $250^{\circ}$  and is distillable; it dissolves in 1.7 parts of water at  $15^{\circ}$ . The *platinochloride* is somewhat soluble in alcohol. The hydrochloride boiled with silver nitrite and water yields trimethyl carbinol.

The boiling points of the iodides and amines of the alcohol-radicles exhibit a constant difference of about  $53^{\circ}$  *c. g.*

		Iodide	Amine	Difference
Ethyl . . . . .	$CH^2CH^3$	72	18.7	53.3
Propyl . . . . .	$CH^2CH^2CH^3$	102.2	49	53.2
Butyl . . . . .	$CH^2CH^2CH^2CH^3$	120.0	76.5	53.4
Isobutyl . . . . .	$CH^2CH(CH^3)^2$	120.6	67.5	53.1
Trimethyl-carbinyl . . . . .	$C(CH^3)^3$	98.5	46	52.5

(Linnemann, *Ann. Ch. Pharm.* clxii. 3).

**BUTYLENE**,  $C^4H^6$ . The number of possible modifications of this and other olefines will be greater or smaller, according as we suppose, on the one hand that their molecules contain either dyad carbon, or free combining units, or on the other hand that they are saturated compounds, having two of their carbon-atoms linked together by two combining units. Thus if butylene be supposed to contain only tetrad carbon-atoms, each pair being united by only one unit of affinity, nine modifications of it may be conceived to exist, four saturated and five unsaturated, viz. those figured in the *First Supplement* (p. 375); and three of these latter, viz. the second, fifth, and eighth, might also be regarded as saturated molecules containing dyad carbon; but if the butylenes are saturated molecules containing only tetrad carbon and having two of these carbon-atoms united by two combining units, then only three modifications are possible, viz.:



These are in fact the only modifications actually known, the first and second being produced by abstraction of HI (action of alcoholic potash) from normal primary butyl iodide,  $CH^2-CH^2-CH^2-CH^2I$ , or from secondary butyl iodide,  $CH^2CH^2-CHI-CH^2I$ , and the third in like manner from isobutyl iodide  $CH(CH^3)^2-CHI$  or from trimethyl-carbinyl iodide  $CI(CH^3)^3$ . The preparation of this third modification (isobutylene) from isobutyl iodide and its conversion into trimethyl carbinol have been already described (p. 210).

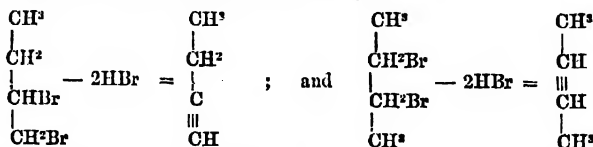
Isobutylene has the same properties whether it be prepared from isobutyl iodide or from trimethyl-carbinyl iodide; that obtained by Butlerow from the former source boiled at  $-6^{\circ}$ , that from the latter at  $-7^{\circ}$  to  $-8^{\circ}$ ; but it was obtained in very small quantity only, and Butlerow regards  $-6^{\circ}$  as the true boiling point. The butylene

obtained by electrolysis of isovaleric (ordinary valeric) acid,  $\text{CH}^2\text{CH}(\text{CH}^3)\text{COOH}$ , is likewise isobutylene, inasmuch as the butyl iodide obtained by combining it with HI, is converted, by treatment with silver oxide and water, into trimethyl carbinol, which, could not be produced from either of the other modifications of butylene (Butlerow *Zeitschr. f. Chem.* [2] vi. 236).

By combining a butylene with 2 atoms of bromine and treating the compound  $\text{C}^4\text{H}^2\text{Br}^2$  with alcoholic potash, it might be expected that a hydrocarbon  $\text{C}^4\text{H}^4$  would be produced, viz. crotonylene; and Caventou indeed states that crotonylene is thus obtained from the butylene produced by exposing the vapour of fusel-oil to heat, (ii.

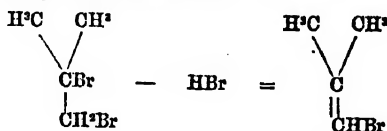
196) which, as Butlerow has shown, is isobutylene. But isobutylene  $\text{H}^2\text{C} - \text{C} \begin{smallmatrix} \text{CH}^3 \\ \text{CH}^3 \end{smallmatrix}$  cannot yield a crotonylene, except by transposition of the atoms, or by the formation of a closed chain, viz.  $\text{H}^2\text{C} = \text{C} \begin{smallmatrix} \text{CH}^2 \\ | \\ \text{CH}^2 \end{smallmatrix}$ . It is more probable, therefore, that

Caventou's butylene was one of the other modifications above mentioned (p. 223), the dibromide of either of which might yield a crotonylene:

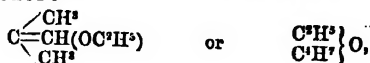


Recent experiments by Prunier (*Compt. rend.* lxxvi, 1410) have shown that the first of these formulae, which is that of ethyl-acetylene, is the true representation of the constitution of crotonylene.

Butlerow, by heating isobutylene dibromide with alcoholic potash, obtains, not crotonylene but isocrotyl bromide  $\text{C}^4\text{H}^3\text{Br}$ :



This compound is a colourless, heavy, aromatic liquid, insoluble or nearly so, in water, boiling at  $88^\circ\text{--}92^\circ$ . Heated in sealed tubes to  $150^\circ$  with concentrated alcoholic potash or crystallised sodium ethylate, it is converted, by exchange of Br for  $\text{OC}^2\text{H}^3$ , into ethyl-isocrotyl ether:



(Butlerow, *Zeitschr. f. Chem.* [2] vi. 523).

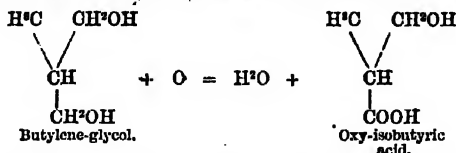
According to Prunier (*Bull. Soc. Chim.* [2] xix. 109) butylene bromide may be obtained, together with some of its homologues, by passing the vapours of light petroleum oils through red-hot tubes, and leading the resulting gases through bottles containing bromine. The results vary with the kind of petroleum employed, the temperature of the tube, the pressure, and the rate of distillation. Petroleum oils boiling below  $50^\circ$  yield much ethylene and but little butylene; whilst oils boiling at  $50^\circ\text{--}80^\circ$  yield butylene and even amylene, together with a considerable quantity of propylene and ethylene.

The most advantageous method of obtaining the propylene and butylene compounds consists in decomposing the vapours of petroleum oils boiling at  $60^\circ\text{--}90^\circ$ , by passing them through a red-hot tube, and conducting the gases thereby produced through a second tube heated to dull redness, and afterwards through bottles containing bromine. The products are separated by fractional distillation, and decolorised by contact with quicklime. There remain in the retort, together with carbonaceous matters, a crystalline body easily extracted by alcohol and ether, and having all the properties of Caventou's tetrabromide of crotonylene,  $\text{C}^4\text{H}^2\text{Br}^4$ , and another body which appears to have the formula  $\text{C}^4\text{H}^2\text{Br}^4$ .

**BUTYLENE GLYCOL**,  $\text{C}^4\text{H}^{10}\text{O}^2 = \text{C}^4\text{H}^9(\text{OH})^2$ .—Ordinary butylene glycol (described in vol. v. p. 789, as tetraenylic alcohol), is obtained from the bromide of



isobutylene (produced by direct combination, or by the action of bromine on secondary butyl iodide), and has the constitution  $\text{CH} \begin{cases} \text{CH}^2\text{OH} \\ \text{CH}^2 \\ \text{CH}^2\text{OH} \end{cases}$ ; when slowly oxidised by dilute nitric acid, it is converted chiefly into butylactic or oxy-isobutyric acid  $\text{C}^4\text{H}^8\text{O}^3$ :



Another modification is produced by the action of sodium-amalgam on acetic aldehyde, the change, which consists in a duplication of the molecule with addition of hydrogen:  $2\text{C}^2\text{H}^3\text{O} + \text{H}^2 = \text{C}^4\text{H}^6\text{O}^2$ , being analogous to that by which benzoic aldehyde  $\text{C}^7\text{H}^5\text{O}$  is converted into benzoin  $\text{C}^8\text{H}^7\text{O}^2$ .

To prepare it, sodium-amalgam is added to an acidulated dilute aqueous solution of aldehyde, and the filtrate is neutralised and distilled, to separate the ethyl alcohol formed at the same time; other by-products are removed by agitation with ether; the aqueous liquid is evaporated almost to dryness, mixed with alcohol, filtered from sodium chloride, and distilled; and the butylene glycol is finally obtained from the portion of higher boiling point by repeated fractional distillation. The product is, however, very small, even under the most favourable conditions.

Butylene glycol thus prepared is a clear syrupy liquid having a sweet but slightly pungent taste; easily soluble in water and alcohol, insoluble in ether; boils at  $203.5^\circ$ – $204^\circ$ . When oxidised by nitric acid, it yields acetic, oxalic, and carbonic acids; with aqueous chromic acid, only acetic and carbonic acids, the oxalic acid undergoing further oxidation. In both cases, also, crotonic aldehyde is formed, together with small quantities of acetic aldehyde.

The formation of crotonic aldehyde by oxidation of this butylene glycol shows that the formula of the latter is  $\text{CH}^2\text{—CH}^2\text{OH—CH—CH}^2\text{OH}$ . Probably the elements of water are first separated, giving rise to crotonic alcohol  $\text{CH}^2\text{—CH=CH—CH}^2\text{OH}$ , which is then oxidised to crotonic aldehyde  $\text{CH}^2\text{—CH=CH—COH}$ . This aldehyde yields the same oxidation-products as the butylene glycol (Kekulé, *Deut. Chem. Ges. Ber.* v. 56).

**BUTYRIC ACID.** Linnemann a. von Zotta (*Ann. Ch. Pharm.* clxi. 175) have prepared normal butyric acid,  $\text{CH}^3\text{CH}^2\text{CH}^2\text{—COOH}$ , from pure fermentation propyl alcohol, by converting this alcohol into iodide, the latter into cyanide by heating it for 30 hours with alcoholic potassium cyanide, and decomposing the cyanide with caustic potash. From the potassium butyrate thus obtained, the acid was separated by neutralisation with hydrochloric acid, evaporation to dryness, and treatment with dry hydrochloric acid gas, and finally purified by distillation over phosphoric anhydride.

Normal butyric acid thus prepared is identical with that which is produced by the fermentation of sugar, as the following comparison will show:—

	Butyric acid prepared by Synthesis	Butyric acid obtained by fermentation of Sugar
Boiling point (corrected) . . . .	$162^\circ$ – $163^\circ$	$162.32^\circ$
Specific gravity at $14^\circ$ . . . .	0.9601	0.9580
Solubility of silver salt $\text{AgC}^4\text{H}^7\text{O}^2$ in water	in 200 parts at $14^\circ$	in 202 parts at $14^\circ$
Solubility of calcium salt $\text{Ca}(\text{C}^4\text{H}^7\text{O}^2)_2 + 2\text{H}^2\text{O}$	in 3.2 parts at $15^\circ$	in 3.5 parts at $14^\circ$
Solubility of barium salt $\text{Ba}(\text{C}^4\text{H}^7\text{O}^2)_2$ (at $100^\circ$ )	in 2.4 parts at $14^\circ$	in 2.43 parts at $14^\circ$
Ethyl ether		
Boiling point . . . .	$121.05^\circ$	$121.07^\circ$
Specific gravity at $18^\circ$ . . . .	0.8953	0.9003

Pure normal butyric acid solidifies in a mixture of salt and snow, and is optically inactive.

2nd Sup.

According to Grünzweig (*Ann. Ch. Pharm.* clxii. 193) it boils at  $157^{\circ}$ – $160^{\circ}$  under a barometric pressure of 716 mm., and its salts exhibit the following solubilities:

100 parts of water dissolve of the

Silver salt	Ag C <sup>4</sup> H <sup>7</sup> O <sup>2</sup>	0.413 part at 16°
Calcium salt	{ unhydr. Ca(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup>	18.1 parts, " 22°
	{ cryst. Ca(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup> + H <sup>2</sup> O	19.61 " 22°
Strontium salt (cryst.)	Sr(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup> + H <sup>2</sup> O	39.2 " 20°
		40.2 " 22°
Zinc salt (cryst.)	Zn(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup> + 2H <sup>2</sup> O	10.7 " 16°

*Isobutylic Normal Butyrate*, CH<sup>3</sup>CH<sup>2</sup>COOH

|  
COO[CH<sup>2</sup>CH(CH<sup>3</sup>)], prepared by treating isobutyl

alcohol with sulphuric acid and normal butyric acid, boils at  $150^{\circ}$ – $155^{\circ}$  (uncorrected) under a pressure of 722 mm. and has a specific gravity of 0.08798 at 0°, 0.86635 at 16°, 0.81838 at 98.44° (Grünzweig).

**Isobutyric acid**, CH(CH<sup>3</sup>)<sup>2</sup>.COOH, is prepared by oxidising isobutyl alcohol with chromic acid mixture. Linnemann and v. Zotta, (*Ann. Chem. Pharm.* clxii. 7), purify it by converting the product into a calcium salt and decomposing this salt with dry hydrochloric acid gas. Pierre a. Puchot (*Ann. Chim. Phys.* [4] xxviii. 363) convert the alcohol by partial oxidation into isobutylic isobutyrate; decompose this ether with potash; distil the resulting potassium isobutyrate with dilute sulphuric acid; and subject the distillate of aqueous butyric acid to a series of fractional distillations, whereby pure isobutyric acid C<sup>4</sup>H<sup>8</sup>O<sup>2</sup> is obtained.

Isobutyric acid boils at  $154.11^{\circ}$  (Linnemann and v. Zotta), at  $155.5^{\circ}$  (Pierre a. Puchot) under a pressure of 760 mm.; at  $149^{\circ}$ – $151^{\circ}$  under a pressure of 716 mm. (Grünzweig). Its sp. gr. is 0.9503 at 20°, (L. and Z.) 0.9697 at 0°, 0.916 at 52.6°, 0.8665 at 99.8°, 0.822 at 139.8° (Pierre a. Puchot). These determinations agree very nearly with those obtained by Markownikoff in 1865 (*1st Suppl.* 378), and show that isobutyric acid is quite distinct in its physical properties from the normal acid; nevertheless, Pierre a. Puchot do not appear to consider the existence of two modifications of butyric acid as distinctly proved\* (see p. 379 of their memoir); and as their acid agrees nearly in physical properties with the butyric acid obtained by fermentation of sugar, which was examined several years ago by Kopp and by Delffs (i. 692), and found to boil at  $156^{\circ}$ , they appear to regard this latter as the pure butyric acid, and the acid of higher boiling point obtained in the same manner, as an impure product. As, however, the butyric acid of fermentation boiling at  $164^{\circ}$  agrees in its properties and those of its derivatives with the acid obtained by oxidation of normal butylic alcohol, it is much more probable that the fermentation acid boiling at  $156^{\circ}$  examined by Kopp and by Delffs was an impure product contaminated with lower homologues.

The metallic isobutyrrates are more soluble than the corresponding normal butyrrates, as may be seen from the following determinations by Grünzweig:

100 parts of water dissolve of the

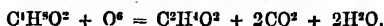
Silver salt	AgC <sup>4</sup> H <sup>7</sup> O <sup>2</sup>	0.928 parts at 16°
Calcium salt	Ca(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup> + 5H <sup>2</sup> O	36.0 " 16°
Strontium salt	Sr(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup> + 5H <sup>2</sup> O	44.1 " 17°
Zinc salt	Zn(C <sup>4</sup> H <sup>7</sup> O <sup>2</sup> ) <sup>2</sup> + H <sup>2</sup> O	17.3 " 19.6°

**Isobutyric Ethers.**—The boiling points and specific gravities of methyl and ethyl isobutyrate have been determined by Pierre a. Puchot; those of isobutyl isobutyrate by Grünzweig:

	Methylic	Ethyllic	Isobutylic
Boiling point.	93° bar. at 760 mm.	113° bar. at 760 mm.	144°–147° bar. at 722 mm.
Specific gravity.	0.9056 " 0°	0.890 " 0°	0.87670 " 0°
"	0.8625 " 38.65°	0.871 " 18.8°	0.86064 " 50°
"	0.805 " 78.6°	0.831 " 55.6°	0.81192 " 95.4°
"	—	0.7794 " 100.1°	—

\* The same disregard of the difference between normal and iso-compounds is exhibited by Pierre a. Puchot in all their researches on the alcohols and acids of the fatty group (see *Compt. Rend.* 1440, 1864; *Chem. Soc. J.* [2] x. 267).

*Oxidation-products of Normal Butyric and Isobutyric Acid.*—Isobutyric acid is oxidised by chromic acid mixture to acetic and carbonic acids:



(Hrlenmeyer, *Zeitschr. f. Chem.* [2] vii. 57).

Now Voel has shown (1st Suppl. 587), that normal butyric acid treated in a similar manner yields propyl butyrate and ethyl butyrate, but no acid containing a smaller number of carbon-atoms. These reactions appear therefore to afford an easy mode of distinguishing the two modifications of butyric acid one from the other.

According to Grünzweig, however, the only difference existing between normal butyric acid and isobutyric acid as to the products of their oxidation by chromic acid lies in the fact that the normal acid is much less readily acted on: the actual products, however, are the same in each case, viz. acetic and carbonic acids; in two experiments with the iso-acid, 98·4 and 100·4 per cent. of the theoretical quantity of carbonic acid were obtained, whilst in three experiments with the normal acid 71, 75, and 106 per cent. were respectively obtained.

*Butyric Acid from various Natural Sources.*—The butyric acid from ordinary butter, and that produced by oxidation of conine (ii. 3) consist of the normal acid, whereas that which exists in the carob bean, or St. John's bread, the fruit of *Ceratonia Siliqua*, is isobutyric acid. When, however, the portion of this fruit left behind on distillation with water is fermented with chalk and cheese, normal butyric acid is produced. The acid in each case was identified by the properties of its silver and calcium salts as given above (Grünzweig, *Ann. Ch. Pharm.* clviii. 117; clxii. 193). Gorup-Besanez found butyric acid in old fruit of the soap-tree (*Sapinda saponaria*), and considers it probable that this acid exists in old tamarinds. Grünzweig found only acetic acid in the latter.

*Crude Butyric Acid of Fermentation.*—Grillone (*Ann. Ch. Pharm.* clxv. 127) has examined the composition of the acid obtained by leaving a mixture of malt, milk, chalk, and minced meat to stand for several weeks. On heating the product to 80°, filtering, precipitating with sodium carbonate, filtering again, evaporating the filtrate to a small bulk, and mixing it with sulphuric acid, a considerable layer of crude fatty acid was obtained, the greater part of which distilled between 156° and 164°, a portion also below 125°, another between 125° and 155°, and another as high as 215°.

The portion boiling below 125° consisted almost wholly of acetic acid; that which distilled between 125° to 155°, of acetic and butyric acids, which were separated by fractional saturation with sodium carbonate and distillation, the butyric acid then passing over, while sodium acetate remained behind. No propionic acid could be detected: a result which agrees with the statement of Linnemann (*Ann. Ch. Pharm.* clx. 224) as to the non-occurrence of propionic acid in crude fermentation butyric acid.

Of the portion distilling above the boiling point of butyric acid, a large fraction went over between 155° and 174°, which seemed to indicate the presence of valeric acid; but this acid was not found. By repeatedly washing the distillate with water, a considerable portion of it was dissolved, and this portion saturated with lime yielded a calcium salt exhibiting very nearly the composition of calcium butyrate, only the traces of the salts of higher acids being present.

The portion insoluble in water distilled between 200° and 205°, and exhibited the composition of caproic acid, the presence of which in crude butyric acid had previously been demonstrated by Stich (*Jahresb.* 1868, 522). The caproic acid thus isolated, yielded an anhydrous barium salt, 100 parts of a saturated solution of which contained at 21°–22°, 8·3 parts of dry salt. Now normal barium caproate is anhydrous, and 100 parts of its solution at 18·5° contain 8·4 parts of dry salt, whereas the caproic acid obtained from fermentation amyl cyanide forms a barium salt which contains 2H<sup>2</sup>O, and dissolves at 18·5° to the amount of 34·65 parts of dry salt in 100 parts of water. The calcium salt of the caproic acid separated as above, contains 1 mol. H<sup>2</sup>O, corresponding therefore with the normal caproate, and not with that of ordinary caproic acid, which contains 3H<sup>2</sup>O. 100 parts of its solution at 21°–22° contain 4·4 parts of dry salt, the solution of normal calcium caproate at 18·5° containing 2·7 parts, and that of the ordinary caproate, 11·3 parts of dry salt. These properties show that the caproic acid contained in crude butyric acid of fermentation is normal caproic acid. No acid was found boiling at a higher temperature than caproic acid.

**BUTYRIC ALDEHYDE, C<sup>4</sup>H<sup>7</sup>O = C<sup>4</sup>H<sup>7</sup>.CHO.** The preparation of normal butyric aldehyde, its physical properties, and its conversion into normal butyl alcohol have been already described in connection with that alcohol (p. 214).

*Isobutyric Aldehyde, CH(CH<sup>3</sup>)<sup>2</sup>.CHO,* may be prepared by distilling calcium isobutyrate with calcium formate, or by oxidation of isobutyl alcohol. By the former process Linnemann and v. Zotta (*Ann. Ch. Pharm.* clxii. 7) obtained isobutyric

aldehyde having a sp. gr. of 0.803 at 20°, and a corrected boiling point of 60°–82°; it dissolved in 9 volumes of water at 20°, and gave crystals with sodium bisulphite, from which it was separated by potash without alteration. By the action of water and sodium-amalgam it is reduced to isobutyl alcohol (p. 214).

A. Pinner (*Deut. Chem. Ges. Ber.* v. 699) prepares isobutyric aldehyde by cautiously oxidising isobutyl alcohol with chromic acid solution mixed with sulphuric acid, to dissolve the chromic hydrate produced; 100 grams of the alcohol,  $\frac{3}{4}$  litre of water, 95 grams of chromic acid, and about 90 c.c. of strong sulphuric acid being employed, and the mixture being only gently warmed. On re-distillation of the distillate in the water-bath, isobutylic isobutyrate is left, and the aldehyde distils over. After treatment with sodium bisulphite (whereby crystals are formed), and drying over calcium chloride, the aldehyde boils constantly at 61°. It forms a difficultly crystallisable compound with ammonia. Potash appears to polymerize the aldehyde, forming a yellow liquid of peculiar aromatic odour, boiling for the most part at 145°–155°.

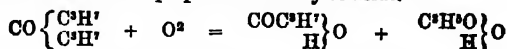
*Sulphuretted hydrogen* forms with isobutyric aldehyde an uncrystallisable oil having an abominable alliaceous odour. With an aqueous solution of isobutyl-aldehyde-ammonia, sulphuretted hydrogen yields isobutyraldine,  $C^{12}H^{12}NS_2$ , as an amorphous mass, very difficult to crystallise. This compound forms with mercuric chloride a compound nearly insoluble in water, amorphous to the naked eye, but crystalline under the microscope. Isobutyric aldehyde shaken with carbon bisulphide, after saturation with concentrated ammonia, forms carboisobutyraldine,  $C^8H^{16}NS_2$ , which is crystallisable and soluble in alcohol and ether, but not in water, and melts at 91°.

*Para-isobutyric Aldehyde.* Barlaglia (*Deut. Chem. Ges. Ber.* v. 105, 2) obtained a polymeric modification of isobutyric aldehyde by passing chlorine into the aldehyde kept at a low temperature. A white crystalline body was thereby produced, insoluble in water, but soluble in alcohol and more freely in ether; melting at 59°–60°, and solidifying at 50°–51°; volatile with vapour of water, and subliming easily without decomposition. It contained no chlorine, and gave by analysis numbers agreeing with the formula  $C^4H^6O$ . Its vapour-density however (105.55 and 103.76 in two determinations) showed that its true formula is  $C^{12}H^{18}O_3$ , the calculated vapour-density for which is 108. This modification is therefore para-isobutyric aldehyde; but the circumstances under which it is formed have not yet been ascertained, as on repeating the experiment, the same body was not produced.

**BUTYRONE.**  $C^4H^6O = CO(C^3H^7)^2$ . *Dipropyl Ketone* (Kurtz, *Ann. Ch. Pharm.* clxi. 205. E. Schmidt, *Deut. Chem. Ges. Ber.* v. 597). Kurtz prepares this body by Chancel's method (1st *Suppl.* 697) namely by distilling pure calcium butyrate in small portions at a time, and submitting the crude distillate to fractional distillation. Agitation with alkaline bisulphites did not separate any of the butyrene, but apparently a mixture of methyl-ethyl ketone and methyl-propyl ketone (1st *Suppl.* 592).

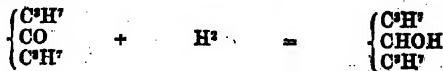
Schmidt heats calcium butyrate mixed with calcium carbonate, to prevent fusion, in a wide iron tube placed in a combustion-furnace, the heat being gradually carried from the back to the front. By operating in this manner in the preparation of butyrene and of other ketones, a much larger product is obtained than when a retort is used, the formation of secondary products being in great part prevented. Calcium carbonate is a more convenient addition, to prevent fluxing, than quicklime, as the latter gives rise to the formation of aldehydes. The crude product is dehydrated by calcium chloride and purified by fractional distillation.

Butyrene boils at 144° and has a sp. gr. of 0.819 at 20° (Schmidt); 0.83 (Chancel). It is converted by nitric acid into nitropropionic acid  $C^3H^5(NO_2)O_2$ , and by oxidation with chromic acid mixture into propionic and butyric acids.



Chlorine acts on butyrene, with evolution of hydrogen chloride, producing a liquid which decomposes on distillation or when left to itself. A similar product is obtained with potassium chlorate and hydrochloric acid. Phosphorus pentachloride also acts readily on butyrene, but the product is not easily separated from phosphorus oxychloride (Kurtz).

On adding sodium in small pieces to butyrene mixed with a very small quantity of water, a strong reaction takes place, and a product is formed containing butyros-pinacone  $C^{14}H^{20}O_2$ , and a secondary heptyl alcohol,  $C^7H^{14}O$ , having the constitution of d propyl carbinol.



This alcohol boils at  $140^{\circ}$ – $150^{\circ}$ , or about  $24^{\circ}$  lower than normal heptyl alcohol or hexyl carbinol  $C^6H^{13}.CH^2OH$ , and about  $12^{\circ}$  lower than the secondary methyl-pentyl carbinol  $CH^3.CHOH.C^3H^{11}$ , both of which have been obtained by Schorlemmer from petroleum oil (see **HEPTYL ALCOHOLS**).

By oxidation with chromic acid mixture, dipropyl carbinol is reconverted into butyrene (Kurtz).

**BUTYRONE-PINACONE**,  $C^{14}H^{30}O^2 = 2C^7H^{14}O + H^2$ , is a crystalline body of sp. gr. 0.87 at  $20^{\circ}$ , melting at  $68^{\circ}$ , resolidifying at  $57^{\circ}$ , and distilling at about  $260^{\circ}$ . It smells and tastes like camphor, dissolves in alcohol and ether, sparingly in water, but does not appear to form a definite hydrate, as is the case with the pinacone of common acetone. By oxidation with potassium dichromate and sulphuric acid, it is reconverted into butyrene (Kurtz).

## C

**CABBAGE.** Analyses of the ashes of the winter cabbage (*Brassica oleracea*, var. *acephala*) have been made by Hofmann (*Landwirthschaftliche Versuchs-Stationen*, xiii. 255). The plant was examined at two stages of its development, as young plants gathered in July, and as mature plants taken in the following January. The young plants averaged 20 cm. in height, and 4.8 grams in weight. The full-grown cabbages were 40–50 cm. in height, and their average weight, after removing the lesser roots, was 236 grams. Of this weight the leaves of the cabbage contributed 188 grams, and the stalk 48 grams. Analysis showed 100 parts in the fresh state to contain:

	Young plant	Winter cabbage	
		Leaves	Stalk
Water . . . .	85.167	20.634	22.458
Dry Substance . . . .	14.833	79.366	77.542
Ash . . . . .	4.257	1.820	1.456
Nitrogen . . . .	.688	3.064	1.661

The composition of the ash in 100 parts was as follows:—

	Young plant	Winter cabbage	
		Leaves	Stalk
Potash . . . . .	30.959	31.728	39.416
Soda . . . . .	—	2.015	3.517
Lime . . . . .	17.710	14.426	12.355
Magnesia . . . . .	4.099	2.845	4.887
Ferric oxide . . . . .	1.565	8.108	1.347
Phosphoric acid . . . . .	7.750	10.093	12.263
Sulphuric acid . . . . .	8.616	6.087	9.203
Silica . . . . .	1.231	1.198	.845
Chlorine . . . . .	8.189	7.640	6.805
Carbonic acid . . . . .	15.175	13.114	7.878
Sand and charcoal . . . . .	6.420	2.692	1.325
	101.714	99.946	99.840

**CADMIUM.** According to Schönn (*Zeitschr. anal. Chem.* x. 391), the action of this metal on nitric acid, which is rapid under ordinary circumstances, is arrested when the cadmium is placed in contact with a sufficiently large quantity of platinum.

When a plate of cadmium and a plate of copper are immersed in a solution of cad-

mium sulphate deprived of air and covered with a layer of oil, only a slight disengagement of hydrogen is observed on the surface of the cadmium, so long as the two plates do not touch, the cadmium being at the same time feebly attacked; but as soon as the plates are made to touch, a deposition of cadmium takes place on the copper plate (Raoult, *Compt. rend.* lxxv. 1103).

**CÆSIUM.** *Occurrence.* The hot spring of Wheal Clifford in Cornwall contains 1·71 part of cesium chloride in a million parts by weight, or 0·12 grain in a gallon, that is about 10 times the quantity contained in the Dürkheim water (Col. Yorke, *Chem. Soc. J.* [2] x. 273).

Sonstadt has detected cesium and rubidium in sea-water and in sea-weed (*Chem. News*, xxii. 25, 44).

*Preparation from Lepidolite.* Stolba (*Dingl. pol. J.* cxvii. 336) heats lepidolite with sulphuric acid (for the preparation of silicofluoric acid) and utilises the residue for the preparation of cesium and rubidium. The residue is boiled with 5 or 6 times its volume of water, to which potassium carbonate is added (40 parts to 100 lepidolite), and the liquid is filtered at the boiling heat. On cooling it deposits a large quantity of potassium-alum containing rubidium and cesium, which may be separated either by Redtenbacher's method (v. 129) or by dissolving the alums in hot strong hydrochloric acid, precipitating the cesium with stannic chloride (1st *Suppl.* 382), and after evaporating the excess of hydrochloric acid from the filtrate, separating the rubidium by silicofluoric acid. The lithium remains in the mother-liquor of the alums.

According to Lecoq de Boisbaudran (*Bull. Soc. Chim.* [2] xvii. 551) a solution containing nothing but alkaline salts may be obtained from lepidolite, more rapidly than by the usual methods, by acting on that mineral with hydrofluoric acid, adding excess of chalk, filtering, precipitating with sodium carbonate and sodium sulphide, and again filtering.

In separating the rubidium and cesium by Bunsen's method, it is better, instead of washing the mixed bitartrates, to dissolve them in just enough hot water, and to stir the solution till it is cold. When the resulting precipitate of rubidium bitartrate is treated in the same way two or three times, it is obtained quite free from cesium.

*Cesio-stannic chloride*,  $2\text{CsCl} \cdot \text{SnCl}_4$ , crystallises in octahedrons or cubo-octahedrons, and has a sp. gr. of 3·308 at 20·5° (referred to water at the same temperature). Before precipitating cesium with stannic chloride, it is necessary to expel ammoniacal salts, inasmuch as ammonio-stannic chloride is insoluble in strong hydrochloric acid. To decompose the cesio-stannic chloride, it is mixed with powdered sal-ammoniac and ignited, whereupon the stannic chloride volatilises (Stolba, *Dingl. pol. J.* cxviii. 255).

**CAFFEINE**,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ . *Extraction from Coffee.*—According to H. Aubert (*Pfäuger's Archiv. f. Physiologie*, v. 589) the largest amount of caffeine is obtained by exhausting the coffee with water, either by percolation or by decoction, evaporating to a syrup, and treating the syrup from five to eight times with chloroform at a temperature near 60°.

Raw beans of the yellow Java kind yielded by this method 0·709–0·849 p.c. while they gave only 0·474 by Garot's method of precipitation with basic lead acetate. When much roasted, coffee loses a certain quantity of caffeine, which sublimates, whereas it loses none by slight roasting. Notwithstanding this, the coffee made in the usual way by percolation from strongly roasted coffee contains rather more caffeine than that made from an equal weight of slightly roasted coffee, as the roasting renders it more easy to extract.

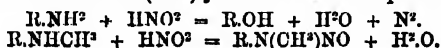
When coffee is prepared by pouring six to ten times its weight of boiling water three or four times over ground coffee, nearly the whole of the caffeine is extracted, hardly one-fifth of it remaining in the grounds. The quantity of caffeine in a cup of coffee prepared from 16½ grams of coffee is about 0·1 to 0·12 gram. A cup of tea prepared in the ordinary way from 5–6 grams of Pekoe tea contains also about 0·1 to 0·12 gram of caffeine.

*Physiological action.*—Caffeine acts upon the spinal cord and causes tetanus in doses of 0·005 gram for a frog, injected subcutaneously; for a rabbit, 0·120 gram (injected into the jugular vein); for cats, 0·200, injected in the same way; and the same quantity for dogs. It has a peculiar action on the muscles of frogs, especially when directly applied to them, causing them to become rigid and white, apparently from coagulation of the myosin. It does not exert this action on the muscles of mammalia. The tetanus is removed by artificial respiration, and if this process is kept up for about a quarter of an hour, no recurrence of the tetanus takes place, even though the respiration is then discontinued, showing that the caffeine is quickly eliminated or destroyed in the organism. Occasionally it produces a paralysis of the hind legs in rabbits. The action of caffeine does not explain the stimulating and reviving action of coffee (Aubert).

**Estimation of Caffeine in Tea-leaves.**—The finely powdered tea-leaves are heated for a few minutes with three times their quantity of chloroform, and the liquid, when cold, is filtered off. The chloroform is then removed by distillation, and the residue is well washed with hot water and filtered; the filtrate, on evaporation, leaves a crystalline mass of caffeine. By this means sufficient caffeine may be extracted from 20 grams of tea to give the characteristic reaction with chlorine-water and ammonia (E. Lioventhal, *Chem. Centralblatt*, 1872, 631).

**Action of Baryta-water on Caffeine and Caffeidine.**—The base  $C^8H^8NO^2$ , obtained, together with formic acid, by the prolonged action of baryta-water on caffeine, was regarded by Schultzen, who discovered it, as different both from sarcosine and from alanine, inasmuch as it did not appear to form double salts with auric chloride or platinum chloride (1st *Suppl.* 383). Rosengarten a. Strecker, however (*Ann. Ch. Pharm.* clvii. 1), have succeeded in preparing both the auro-chloride and the platinum-chloride of this base, and find that they are identical in composition and properties with the corresponding salts of sarcosine or methyl-glycocine,  $CH^3(NHCH^3).COOH$ . The base obtained from caffeine also dissolves cupric oxide on boiling, and the liquid on cooling yields well-defined rhombic crystals of the compound  $(C^8H^8NO^2)_2Cu + H^2O$ , identical with those obtained in like manner from sarcosine prepared from creatine (v. 107). Moreover, when its aqueous solution is mixed with cyanamide and a little ammonia, it is converted into creatine.

A further proof of the identity of this base with sarcosine is afforded by the fact, noticed by Schultzen, that when treated with nitrous acid it yields a nitroso-compound, the calcium salt of which is represented by the formula  $[C^8H^8(NO)NO^2]Ca + H^2O$ , inasmuch as compounds which contain the group  $NH^2$  are usually converted by nitrous acid into oxy-compounds (e.g. alanine into lactic acid), whereas those which contain the methylamine residuum  $NH(CH^3)$  yield nitroso-compounds; thus:—



The equation representing the decomposition of caffeine by baryta-water is



Creatine similarly treated yields sarcosine, carbon dioxide, and ammonia, but neither formic acid nor methylamine.

**CAJUPUT OIL.** The presence of copper in cajuput oil was first observed by Guibourt, who found, on examination of a certain specimen, as much as 0.0274 p.c. (1st *Suppl.* 710); at the present day, however, the actual occurrence of copper in well-authenticated samples has been much doubted, more especially since the investigations of later chemists, have, as a rule, failed to corroborate the experiments of Guibourt. On the other hand, E. Histed, having carefully examined numerous specimens of cajuput oil from various commercial sources, has obtained in every instance abundant indications of the presence of copper. He finds, moreover, that cajuput oil, though naturally possessing a green colour, becomes perfectly colourless when redistilled. This colourless oil acts readily upon metallic copper, and in a few days re-acquires a green colour; the quantity of copper dissolved is, however, too small to render the oil unfit for medicinal use (*Pharm. J. Trans.* [3] ii. 804).

**CALAMUS OIL.** When the volatile oil obtained from the root of *Acorus Calamus* is submitted to fractional distillation, the boiling point rises from  $140^\circ$  to  $280^\circ$ , and the fraction passing over at  $170^\circ$  yields, on careful redistillation, a considerable quantity of product boiling at  $158^\circ$ – $159^\circ$ . The oil thus obtained is a hydrocarbon (calamone) having the composition  $C^{10}H^{16}$ . It smells like turpentine, is transparent, soluble in alcohol and ether, and has a specific gravity of 0.8793 at  $0^\circ$ . It unites with hydrochloric acid, forming a crystalline mass which melts at about  $65^\circ$ .

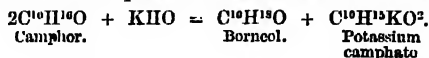
The oils of higher boiling point yield by rectification a bluish liquid boiling at  $250^\circ$ – $255^\circ$ . The colour disappears on boiling with sodium, and the hydrocarbon then boils at  $255^\circ$ – $258^\circ$ . This hydrocarbon has also the composition  $C^{10}H^{16}$ ; it dissolves slightly in alcohol, easily in ether, and does not combine with hydrochloric acid (Kurbatow, *Deut. Chem. Ges. Ber.* vi. 1210).

**CALCEPAR.** See CARBONATES, (p. 267).

**CALCIUM CHLORIDE.** *Supersaturated solution.*—A solution of 350–400 grams of crystallised calcium chloride in 50 c.c. of water, or of 200 grams of the anhydrous salt in 260 c.c. of water, prepared warm, may be shaken after cooling, either alone or with fragments of glass, without crystallising, but solidifies as soon as it is touched with a crystal of calcium chloride. The same solution when cooled to  $5.8^\circ$  begins to crystallise, the temperature then rising to  $25^\circ$ – $30^\circ$ . A solution con-

taining 55 p.c.  $\text{CaCl}_2$  deposits at about  $15^\circ$  large plates of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ , which do not induce the crystallisation of the supernatant liquid. This solution in passing from the liquid to the solid state undergoes at  $70^\circ$  a contraction amounting to 0.0832 of its volume (E. Lefebvre, *Compt. rend.* lxx. 684).

**CAMPHIC ACID.**  $\text{C}^{10}\text{H}^{16}\text{O}_2$ .—An acid produced, together with borneol, by heating camphor with alcoholic potash in sealed tubes to  $180^\circ$ – $200^\circ$ :

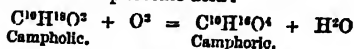


When separated by acids from the potassium salt, it forms a more or less coloured, nearly solid resin, and the solutions of its salts when evaporated leave only uncrystallisable syrups or amorphous masses (Berthelot, *Ann. Ch. Phys.* [3] lvi. 94). Wheeler (*Ann. Ch. Pharm.* cxlvi. 84) obtained the lead salt as a white insoluble powder which gave by analysis 38.77 p.c. lead, the formula  $\text{Pb}(\text{C}^{10}\text{H}^{15}\text{O}_2)_2$  requiring 38.27 p.c. The *oxycamphor*, which Wheeler obtained by heating monochlorocamphor with alcoholic potash, has the same composition as camphic acid (1st Suppl. 387).

Kachler (*Ann. Ch. Pharm.* clxii. 268) denies the existence of camphic acid as a distinct compound. By boiling camphor ( $\frac{1}{2}$  lb.) with alcoholic potash in a flask fitted with a condensing tube for 250 hours, treating the cooled mass with water, and straining the liquid through a cloth, he obtained a milky liquid containing potassium camphate and unaltered camphor; the latter was removed by ether, and a clear solution thereby obtained from which sulphuric acid threw down a flocculent resinous mass of crude camphic acid. This, when subjected to prolonged boiling with water, yielded a distillate containing campholic acid, and as residue, a hard, brittle, slightly acid resin, which, when heated with potassium hydrate, gave off a large quantity of camphor vapour, leaving a difficultly oxidisable residue. Hence Kachler concludes that the so-called camphic acid is nothing but a mixture of campholic acid with an acid resin, probably formed by condensation and oxidation of several molecules of camphor. To this Berthelot replies (*Bull. Soc. Chim.* [2] xvii. 390) that Kachler's failure in obtaining a definite product by the action of alcoholic potash on camphor probably arose from his having operated in an open vessel, whereas Berthelot himself obtained camphic acid by heating the materials in sealed tubes. J. Montgolfier (*ibid.* xviii. 114) heated some of the camphic acid prepared by Berthelot with water, without obtaining a trace of campholic acid; neither did the camphic acid when treated with nitric acid, yield any camphoric acid, as it should have done had it contained campholic acid. The question as to the existence of camphic acid as a definite compound must therefore be regarded as at present undecided. According to Montgolfier, camphic acid is almost insoluble in cold, slightly soluble in boiling water, and has a specific rotatory power of  $+15.8^\circ$ .

**CAMPHOLIC ACID,**  $\text{C}^{10}\text{H}^{18}\text{O}_2$ . This monobasic acid, originally obtained by Delalande by passing camphor-vapour over red-hot potash-lime (1st Suppl. 726), is best prepared by Malin's process (1st Suppl. 386), namely by the action of potassium on a hot solution of camphor in petroleum boiling at about  $130^\circ$ . The potassium campholate thus produced yields, when decomposed by sulphuric acid, a quantity of campholic acid amounting to 20–22 p. c. of the camphor employed.

Campholic acid crystallises from ether-alcohol in soft nodular groups of irregular-shaped laminae. It is nearly insoluble in cold water, melts below the boiling point of water, then dissolves to a slight extent, and separates in crystalline flocks on cooling. It volatilises with vapour of water, becomes buttery at  $80^\circ$ , and melts in capillary tubes at  $96^\circ$ , (Delalande gives  $80^\circ$  as the melting point). Nitric acid converts it, first into camphoric, then into camphoronic acid:



and



With bromine and water, campholic acid yields, first camphoric acid, then bromo-camphoric anhydride,  $\text{C}^{10}\text{H}^{14}\text{BrO}_2$ , and lastly oxy-camphoric anhydride  $\text{C}^{10}\text{H}^{12}\text{O}_4$  (p. 236). Phosphorus pentachloride converts it into campholic chloride  $\text{C}^{10}\text{H}^{17}\text{OCl}$ , which is an oil decomposed by water. The calcium salt when distilled yields campholene  $\text{C}^{10}\text{H}^{16}$ . The substance called *campholone* obtained by this process by Delalande, who assigned to it the formula  $\text{C}^{10}\text{H}^{16}\text{O}$ , was probably campholene mixed with some oxidised body (Kachler, *Ann. Ch. Pharm.* clxii. 259).

Most of the campholates are crystallisable. The potassium salt  $\text{C}^{10}\text{H}^{17}\text{KO}$  and the sodium salt  $\text{C}^{10}\text{H}^{17}\text{NaO}$  obtained by dissolving the acid in the dilute alkalis are precipitated, as flocculent or sandy crystalline powders, on mixing their mother-liquors.



dilute solutions with strong caustic alkali. The other salts are formed from the ammonium salt by double decomposition; the *barium, calcium, zinc, and magnesium salts* separate in microscopic needles; the *copper salt* as an amorphous light-green precipitate; the *silver salt*,  $C^{10}H^{17}AgO_2$ , as a white precipitate not much affected by exposure to light. Ethyl campholate is not formed by the action of hydrogen chloride on an alcoholic solution of the acid.

**CAMPHOR,  $C^{10}H^{16}O$ . Artificial Formation.** When cymene (prepared from turpentine-oil or from citrene) is oxidised with potassium chromate and sulphuric acid, in a flask provided with an upright condensing tube, a small quantity of a white crystalline substance sublimes in the tube, having the appearance, odour, and composition of ordinary camphor. The substance thus obtained was found to boil at  $162^\circ$ , common camphor boiling at  $175^\circ$ ; the difference was probably due to impurity, as the quantity of substance obtained was too small to admit of purification (Oppenheim, *Deut. Chem. Ges. Ber.* v. 631).

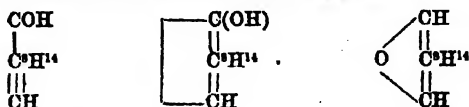
**Action of Nitric Acid.** When camphor is heated in a retort with nitric acid of sp. gr. 1.37, there is formed, besides camphoric and camphretic (camphoronic) acids, a volatile liquid which floats on top of the acid liquid condensed in the receiver. This substance is more or less decomposed by washing with water or by distillation, and can therefore be purified from absorbed nitrous vapours only by passing through it a stream of dry air or carbonic acid gas. It has the composition of a *nitrate of camphor*  $2C^{10}H^{16}O.N^2O^2$ , analogous to that of cinnamic aldehyde  $2C^9H^8O.N^2O^2$ . Water immediately decomposes it, forming camphor and nitric acid. Caustic potash, on the other hand, does not affect it (Kachler, *ibid.* iv. 380).

The mother-liquors obtained in the preparation of camphoric acid deposit, after long standing, a crystalline body, which by recrystallisation from water, is obtained in thin transparent rhombs having the composition of tetranitro-camphor  $C^{10}H^{12}(NO^2)^4O$ . It volatilises by slow evaporation, and explodes when quickly heated. It dissolves sparingly in cold water, easily in alcohol, ether, and ammonia, and forms with the latter a salt which is precipitated by lead acetate and silver nitrate (Schlebusch, *ibid.* iii. 591).

**Action of Ammonium Sulphide.**—Camphor heated for eight or ten hours to  $130^\circ$  with alcoholic ammonium sulphide, yields a product which crystallises from hot alcohol in feathery crystals and appears to have the composition  $C^{10}H^{18}S$ . (Schlebusch).

#### Constitution of Camphor and its Derivatives.

As camphor, by abstraction of water, yields a homologue of benzene, viz. cymene, it probably contains a 6-carbon nucleus to which the remaining four carbon-atoms are attached in lateral chains. V. Meyer, however (*Deut. Chem. Ges. Ber.* iii. 116), supposes that the carbon-atoms in this nucleus do not form a closed chain, and that in the oxidation of camphor it is not the lateral chains which are attacked (as in that case hydrogen would be removed); but that the oxidation appears to be wholly confined to two of the six carbon-atoms of the nucleus. Moreover, he considers that the carbon-atoms which yield carboxyl by oxidation, cannot be attached to the same carbon-atom of the camphor-molecule, as in that case the camphor could not be converted by dehydration into a homologue of benzene. On this view then, there remain only three formulæ by which the constitution of camphor may be expressed:



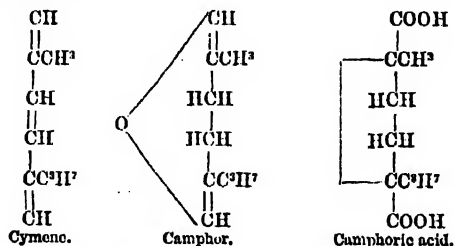
The nucleus  $C^6H^{14}$  (which includes the 4 carbon-atoms present as lateral chains) is in these formulæ quadrivalent; in camphoric acid, on the other hand, it is bivalent, two of its units of affinity neutralising one another (*vid. infra*).

The first of these formulæ represents camphor as an aldehyde, which is the view proposed some time ago by Berthelot; but as Tollens and Fittig have shown that it does not exhibit any of the properties of an aldehyde (*1st Suppl.* 386) this formula must be rejected. According to the second formula, camphor contains the group OH, and should therefore exhibit alcoholic characters. It differs, however, from the alcohols by its complete indifference to acids; indeed Berthelot has shown that it may be separated from borneol, which is a decided alcohol, by its indifference to stearic acid and other acids. Moreover, it is not altered in the slightest degree by prolonged heating with acetyl chloride, and when its alcoholic solution saturated with hydrogen

chloride is left for weeks in sealed tubes, not a trace of ethylated camphor is produced. From these results it may be inferred that camphor does not contain the group OH, and therefore that it cannot be represented by the second of the above formulae.

There remains then only the third formula  $O \begin{array}{c} \diagup CH \\ || C^6H^{14} \\ \diagdown CH \end{array}$  as the representative of its

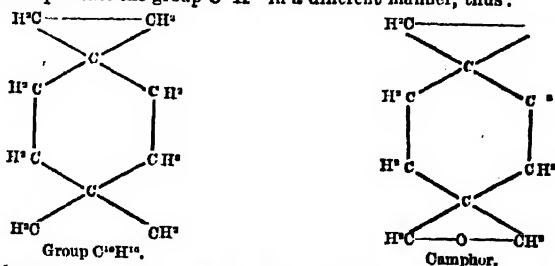
constitution. The constitution of the nucleus  $C^6H^{14}$  may be inferred from that of cymene, which, according to the experiments of Fittig, Köbsch and Jilke, has the constitution of methyl-propyl- (or isopropyl-) benzene (1st Suppl. 302). This hydrocarbon, together with camphor and camphoric acid, may accordingly be represented by the following formulae:



Borneol and campholic acid may be represented by the following formulae:

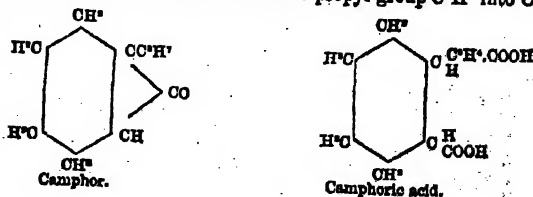


Hlasiwetz (*ibid.* 539) agrees with Meyer as to the position of the oxygen-atom in camphor, but represents the group  $C^{10}H^{16}$  in a different manner, thus:

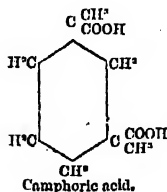
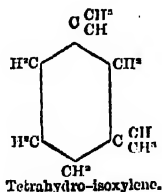


On the other hand, Kachler (*Ann. Ch. Pharm.* clxix. 185) regards camphor as a ketonic body, containing the group CO and formed on the closed ring of the benzene nucleus. The ketonic character is inferred from its conversion into borneol  $C^{10}H^{16}O$ , by the action of nascent hydrogen, which is similar to that of acetone into isopropyl alcohol, and by its reaction with bromine, chlorine, phosphorus pentachloride, and hydriodic acid, which are exactly analogous to those of acetone.

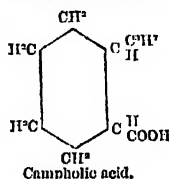
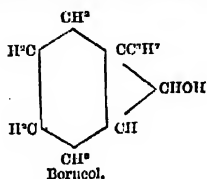
Kachler represents camphor and camphoric acid by the following formulae, the formation of the latter by oxidation of camphor being supposed to consist in the conversion of the group CO into COOH and of the propyl group  $C^3H^7$  into  $C^3H^7COOH$ :



Wredon (*Deut. Chem. Ges. Ber.* v. 1106) finds that the hydrocarbon  $C^8H^{14}$  obtained from camphoric acid is converted by fuming nitric acid into trinitro-isoxylene; whence it would appear that camphoric acid is tetrahydro-isoxylene-bicarbonic acid:



Borneol is related to camphor in the same manner as isopropyl alcohol to acetone; and campholic acid may be represented as the mono-carbonic acid of a propyl-hexylene.

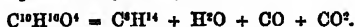


**CAMPHORIC ACID**,  $C^{10}H^{16}O^4 = C^8H^{14} \begin{Bmatrix} COOH \\ COOH \end{Bmatrix}$  Wredon (*Ann. Ch. Pharm.*

clxiii. 323) prepares this acid by dissolving 160 grams of camphor in 2 litres of nitric acid, sp. gr. 1.27 (2 vols. of the strong commercial acid to 1 vol. of water) and heats the solution for 50 hours in a large flask standing in a water-bath and having cemented to its mouth a long condensing tube, bent at right angles and leading into the chimney. Camphor thus treated yields more than half its weight of purified camphoric acid.

Camphoric acid melts at  $174^{\circ}$ – $176^{\circ}$ , not  $60^{\circ}$  and  $70^{\circ}$ , as commonly stated (V. Moyer, *Deut. Chem. Ges. Ber.* iii. 116).

Camphoric acid heated with hydriodic acid (sp. gr. 1.7) to  $200^{\circ}$  for not more than eight hours—the gases formed ( $CO$  and  $CO_2$ ) being allowed to escape from time to time—yields a heavy iodised oil of variable boiling point, from which, by distillation over quicklime and subsequent treatment with sodium, the hydrocarbon  $C^8H^{14}$  is obtained. The decomposition is represented by the equation:

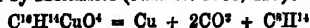


By further heating the iodised oil ( $C^8H^{14}.HI?$ ) with hydriodic acid to  $200^{\circ}$  for nine hours, the hydrocarbon  $C^8H^{14}$  is produced (Wredon, *Zeitschr. f. Chem.* [2] vii. 120).

Camphoric acid distilled with excess of lime, splits up into water and camphoric anhydride  $C^{10}H^{14}O^3$ , which at a higher temperature is further decomposed by the lime yielding phorone:



Cupric camphorate when strongly heated gives off carbon dioxide and the hydrocarbon  $C^8H^{14}$ , as first observed by Moitissier (*Jahresb.* 1866, 428):



(V. Moyer, *Zeitschr. f. Chem.* iii. 498).

**Meso-camphoric acid.** Camphoric acid has hitherto been known in four isomeric modifications: viz. dextro-camphoric acid (the ordinary acid); levo-camphoric acid, an optically inactive acid (para-camphoric acid) obtained by mixing equivalent quantities of these two active acids; and an insoluble modification, also optically inactive, which is formed by decomposing para-camphoric ether with boiling potash-ley (1st Suppl. 389).

A new inactive modification—meso-camphoric acid—related to dextro-camphoric acid in the same manner as meso-tartaric acid to dextro-tartaric acid—is formed by the regulated action of concentrated hydriodic or hydrochloric acid on the ordinary dextro-acid, e.g. when this acid is heated to  $140^{\circ}$  in portions of 5 grams each with 20 c.c. of fuming hydrochloric acid (at  $200^{\circ}$  the hydrocarbon  $C^8H^{14}$  is obtained).

Meso-camphoric acid crystallises from water in felted needles or nodules. It crystallises unaltered from solution in strong sulphuric acid, whereas ordinary camphoric acid is converted thereby into the anhydride. By prolonged action of sulphuric acid a sulpho-acid is formed exhibiting all the properties of Walter's sulpho-camphoric acid.

Meso-camphoric acid when heated yields a sublimate of camphoric anhydride. Its ammonium salt forms an amorphous transparent mass, the calcium salt has been obtained only in pellicles.

When meso-camphoric acid is repeatedly crystallised from water, or, better, from dilute alcohol, or when its aqueous solution is boiled for a fortnight with hydrochloric acid, it is converted into a new modification, having all the properties of common camphoric acid, with the exception of being inactive. By treating it with an excess of concentrated hydriodic acid, the hydrocarbons  $C^{10}H^{14}$ ,  $C^{10}H^{16}$ ,  $C^{10}H^{18}$  are formed, (Wreden, *Zeitschr. f. Chem.* [2] vii. 419).

*Substitution-products of Camphoric Anhydride  $C^{10}H^{14}O^2$ .*

**Bromo-camphoric Anhydride,  $C^{10}H^{12}BrO^2$ .**—When 1 mol. bromine is heated with 1 mol. camphoric acid in presence of water to  $170^\circ$  and the mixture is left to cool, long prismatic crystals, probably having the composition  $C^{10}H^{16}O^2Br^2$ , are obtained, which when exposed to the air are slowly resolved into bromine and camphoric acid. In the absence of water the reaction takes a different course, bromocamphoric anhydride being formed:



To prepare this body, a mixture of 12 grams camphoric anhydride and 18 grams dry bromine is heated in a sealed tube for about three hours at  $130^\circ$ — $140^\circ$ . The contents of the tube are then washed out with ether, and the white powder so obtained is re-crystallised from chloroform. It is less soluble in ether than camphoric anhydride; crystallises from strong boiling alcohol in small needles, but with partial decomposition. It dissolves undecomposed in 60 per cent. spirit at a temperature of  $60^\circ$ , and is readily soluble in chloroform, from which it may be obtained in transparent prismatic crystals. It blackens when heated to  $100^\circ$ , and is not attacked by phosphorus pentachloride under the ordinary atmospheric pressure. It does not exhibit the usual behaviour with water characteristic of anhydrides; for on treatment with water or alcohol, the bromine becomes replaced by the OH or  $OC^2H^5$  group. More highly brominated products of camphoric anhydride have not been obtained (Wreden, *Ann. Ch. Pharm.* clixiii. 330; *Zeitschr. f. Chem.* [2] vii. 97).

**Oxycamphoric Anhydride,  $C^{10}H^{14}O^4 = C^{10}H^{12}(OH)O^2$**  (also called *Camphanic acid*) is prepared by heating bromocamphoric anhydride with water in a flask connected with an inverted condenser. If the bromanhydride contains camphoric anhydride, the product will also contain camphoric acid. To remove this, it is converted into the lead salt, whereupon insoluble lead camphorate is formed, which may be filtered off, and the oxyacid then set free by sulphuric acid (Wreden). It is also produced by the action of bromine and water on campholic acid (Kuchler, *ibid.* lxxii. 264):



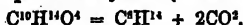
Oxycamphoric anhydride melts at  $201^\circ$ , and if heated for some time at  $200^\circ$  begins to decompose; it is soluble in ether and alcohol, also in water, but in this case it first melts; it also separates as an oil on cooling from a hot saturated aqueous solution. It crystallises with one or two molecules of water, but becomes anhydrous on standing over sulphuric acid in a vacuum.

Oxycamphoric anhydride forms salts, all of which with the exception of the sodium salt, are crystalline and soluble in water. The lead salt is difficultly soluble even in boiling water; the barium and silver salts decompose when heated with water; a volatile oil escapes while barium carbonate or silver remains. The cadmium salt,  $Cd(C^{10}H^{12}O^4)^2 + 3aq.$ , crystallises in transparent prisms which lose their water at  $100^\circ$ . The ether  $C^{10}H^{12}(C^2H^5)O^4$ , produced by passing hydrochloric acid gas into a solution of oxycamphoric anhydride in absolute alcohol, or by heating bromocamphoric anhydride with alcohol to  $160^\circ$  in sealed tubes, forms prismatic needles, which melt at  $63^\circ$  and sublime below  $100^\circ$ ; it dissolves readily in alcohol, ether, chloroform, and carbon sulphide, slightly in boiling water, which is without action on it. It is saponified by heating with potash-solution.

Phosphorus pentachloride converts oxycamphoric anhydride into the corresponding chloranhydride from which water regenerates oxycamphoric anhydride.

On heating the calcium salt of oxycamphoric anhydride, an oil is obtained, which

after heating with sodium in a sealed tube to  $100^{\circ}$ , boils at  $118^{\circ}$ — $120^{\circ}$ , has the composition  $C^6H^{10}$ , and the vapour-density 3.75 (calculated 3.8):



The same body is formed by heating oxycamphoric anhydride with water to  $180^{\circ}$ , carbonic anhydride and carbonic oxide being evolved; probably also by heating the anhydride to  $150^{\circ}$  with strong hydriodic acid (Wreden).

It will be seen from the results above described that oxycamphoric anhydride exhibits the characters of an acid, hence the name *camphonic acid*; it is the first representative of a new class of acids not containing carboxyl (Wreden, *loc. cit.*).

**Amidecamphoric Anhydride and acid**,  $C^6H^{10}(NH^2)O^3$ , is formed by dissolving bromocamphoric anhydride,  $C^6H^{10}BrO^3$ , in aqueous ammonia at  $150^{\circ}$ . It crystallises in needles, is sparingly soluble in boiling water and cold alcohol, but dissolves readily in boiling alcohol. When heated it begins to sublime at  $150^{\circ}$ , and melts at  $208^{\circ}$ . Nitrous acid converts it into oxycamphoric anhydride,  $C^6H^{10}(HO)O^3$ . The same compound is formed by boiling it with concentrated alkalis, whilst dilute alkalis produce *amidecamphoric acid*,  $C^6H^{10}(NH^2)O^4 + H^2O$ , which is more soluble in alcohol than the anhydride, and crystallises in small shining prisms. It loses its water at  $85^{\circ}$ , and between  $85^{\circ}$ — $160^{\circ}$  is changed into the anhydride, which is also formed by the action of nitrous, or of concentrated hydrochloric and sulphuric acids. The *calcium salt*  $Ca(C^6H^{10}NH^2O^4)^2 + 2H^2O$  forms transparent prisms, and dissolves readily in water; a normal calcium salt could not be obtained. The *copper salt* crystallises from water in blue shining needles; the *cadmium salt* in iridescent pellicles.

**CAMPHORONIC ACID**,  $C^6H^{10}O^3$  (Kachler, *Ann. Ch. Pharm.* clix. 281). This acid is formed, together with camphoric acid, by the action of nitric acid on camphor. The syrupy concentrated mother-liquor from which the camphoric acid has separated deposits crystals, after standing for some months, the mass finally becoming semi-solid; and, on subjecting this mass to strong pressure, and recrystallising the solid portion from water, after decoloration with animal charcoal, camphoronic acid is obtained in minute pearly crystals, very soluble in water, alcohol and ether, but almost insoluble in benzene and carbon sulphide. The aqueous solution has an acid taste and reaction and decomposes carbonates, forming two classes of salts, in which 2 and 3 atoms of hydrogen are replaced by metals. The acid itself, when air-dry, has the composition  $C^6H^{10}O^3$  or  $C^6H^{10}O^4.H^2O$ . It does not give off water at  $100^{\circ}$ , but when heated to  $110^{\circ}$  it begins to fuse and loses water, giving an anhydrous compound which melts at  $115^{\circ}$ , and distils unaltered at a slightly higher temperature; both the distilled product and the substance melting at  $115^{\circ}$  have the composition  $C^6H^{10}O^3$ .

Camphoronic acid is not precipitated in the cold by any metallic salt, except lead-salts, which give a white precipitate. On heating it with solution of *cupric acetate*, a copious light green precipitate is formed, which redissolves completely as the liquid cools.

The *bibasic ammonium salt* gives off both water and ammonia at  $100^{\circ}$ ; dried *in vacuo* it contains  $C^6H^{10}(NH^2)O^3 + H^2O$ . The *bibasic barium and zinc salts* are obtained by treating the acid with the carbonates of these metals; dried at  $170^{\circ}$  they contain  $C^6H^{10}BaO^3$  and  $C^6H^{10}ZnO^3 + H^2O$ , the latter not losing its water even at  $200^{\circ}$ .

By boiling a solution of the acid saturated with ammonia with *barium chloride*, an insoluble sandy crystalline powder is precipitated which will bear washing with water; this is a tribasic salt, and has the composition  $Ba^2(C^6H^{10}O^3)^2 + 2H^2O$ , the water of crystallisation being lost at  $185^{\circ}$ ; the formation of this sandy precipitate on boiling serves as a qualitative test for the acid, and also as a means of preparing the pure acid from the syrupy mother-liquors in the first instance, by decomposition of the salt with dilute sulphuric acid and exhaustion with ether.

A *tricalcio salt*  $Ca^3(C^6H^{10}O^3)^2 + 4H^2O$  is obtained in needle-shaped crystals by saturating the acid with calcium carbonate.

A *tricupric salt* is formed, as above mentioned, by heating the solution of camphoronic acid with cupric oxide, and separates as a light green powder, which redissolves on cooling, but may be washed with hot water; its composition is  $Cu^3(C^6H^{10}O^3)^2 + 4H^2O$ . The liquid filtered from this and concentrated, deposits after some time a bluish green salt of darker colour than the preceding, and having, when dried, the composition  $Cu^3(C^6H^{10}O^3)^2 + 2H^2O$ .

The *lead and silver salts*, which are obtained by precipitation, the latter from the ammonium salt, are decomposed by washing; the silver salt appears to be tribasic. The *potassium and sodium salts* are extremely soluble, and have not been obtained in definite forms.

An alcoholic solution of camphoronic acid saturated with gaseous hydrogen chloride,

deposits an oil which yields by distillation, a *mono-ethylic ether*  $C^6H^{11}(C^2H^5)O^2$ , boiling at  $302^\circ$ .

The calcium salt, mixed with quicklime and distilled, gives a thick product, from which, by rectification, a clear and perfectly volatile substance  $C^6H^{12}O$ , may be isolated, formed by the reaction,  $C^6H^{12}O^2 = 2CO^2 + C^6H^{12}O$ . This formula requires a vapour-density = 3.86; the numbers found in two determinations were 3.69 and 3.74.

Camphoronic acid, heated with three times its weight of caustic potash, is completely decomposed; and by distillation of the product with dilute sulphuric acid, a distillate containing *butyric acid* is obtained, the reaction being,  $C^6H^{12}O^2 + 12H + H^2O = 2C^4H^8O^2 + CO^2$ .

Camphoronic acid is a product of the oxidation of camphoric acid, and is always formed when the latter is boiled with nitric acid till camphoric acid no longer crystallises out on cooling. If the liquid be then evaporated, an acid syrup is obtained, exhibiting all the properties of Schwannert's camphrotic acid (1st Suppl. 390). The acid so called appears, however, to be nothing but a mixture of camphoronic and camphoric acids, the former of which may be separated as a barium salt in the manner above described; and if the filtrate be then acidulated with sulphuric acid and agitated with ether, and the ethereal solution evaporated, a syrupy liquid resembling the so-called camphrotic acid is obtained, which, sometimes merely on standing, but more frequently after dilution with water, deposits crystals of camphoric acid. The mother-liquors, if again treated with ammonia and barium chloride, yield an additional quantity of camphoronic acid.

*Oxycamphoronic acid*  $C^6H^{12}O^6$  is formed when a mixture of 1 mol. air-dried camphoronic acid,  $C^6H^{12}O^5.H^2O$ , and 2 atoms of bromine is heated to  $130^\circ$  for two hours in sealed tubes:  $C^6H^{12}O^5 + Br^2 = 2HBr + C^6H^{12}O^6$ . On opening the tubes a large quantity of hydrogen bromide escapes, and a syrupy liquid is left, which dissolves almost wholly in water, forming a solution which, after concentration, deposits hydrated oxycamphoronic acid,  $C^6H^{12}O^6.H^2O$ , in large crystals which give off their water at  $100^\circ$ .

The crystals, which are obtained particularly large and fine by redissolving the acid in water, decolorising the solution with animal charcoal, and leaving it to evaporate over sulphuric acid, are monoclinic, having their axes  $a : b : c = 1.4918 : 1 : 0.98075$ , and the angle  $ac = 86.50$ . Observed faces  $\infty P \infty . 0P . +P \infty . \alpha P . (\infty P \infty) . -\frac{1}{2}P \infty$ .

Oxycamphoronic acid has a pure and pleasant sour taste: it dissolves easily in water, alcohol, and ether. The dehydrated acid begins to melt at  $210^\circ$ , solidifies in the crystalline form on cooling, and may be distilled without alteration. It is a strong acid, decomposing carbonates with facility, and forming salts in which 2 or 3 atoms of hydrogen are replaced by metals. Like camphoronic acid, it is not directly precipitated by any metallic salts, excepting basic lead acetate. It does not exhibit the reaction of camphoronic acid with cupric acetate, but behaves in a similar manner to that acid, when its solution saturated with ammonia is heated with barium chloride, excepting that the precipitated barium salt is bibasic instead of tribasic, as in the case of camphoronic acid.

An *acid potassium salt*  $C^6H^{11}KO^4 + H^2O$  is obtained in small shining crystals by saturating the half of a solution of the acid with potassium carbonate, then adding the other half, and concentrating. The *neutral salt*  $C^6H^{10}K^2O^6$ , obtained by complete saturation, dries up in a vacuum to a gummy very hygroscopic mass. The *barium salt*  $C^6H^{10}BaO^6$ , prepared as above, forms nacreous laminae. The *calcium salt*  $C^6H^{10}CaO^6$  dries up in a vacuum to a fissured mass which may be triturated to a chalky powder. The *lead salt* formed by precipitation has, when dried at  $120^\circ$ , the composition  $Pb(C^6H^9O^6)^2 + 2H^2O$ ; it is the only trimetallic oxycamphoronate yet obtained. The *silver salt*  $C^6H^{10}Ag^2O^6$  is obtained by precipitation in white flocks; it is moderately soluble in water, and decomposes partially during washing and drying.

Oxycamphoronic acid is not formed from anhydrous camphoronic acid by the action of bromine; neither is any bromine substitution-compound obtainable from either acid. Fused caustic potash acts on both acids alike; both are but little attacked by nitric acid, and are unaltered by treatment with sodium-amalgam.

**CAMPHERENE.**—This name was given by Schwannert to a product isomeric with phorone,  $C^6H^{14}O$ , which he obtained by the action of sulphuric acid upon camphor (1st Suppl. 290). According to Kachler, however (*Ann. Ch. Pharm.* cxlvi. 79), the substance thus obtained is not a definite compound, but a mixture of phorone with a hydrocarbon which raises its boiling point to  $230^\circ$ – $235^\circ$  (pure phorone from camphoric acid boiling at  $208^\circ$ ). Camphrene prepared according to Schwannert's directions gave by analysis 1 p.c. less carbon than that required by the formula  $C^6H^{14}O$ , and was resolved by fractional distillation into a portion boiling at a considerably lower temperature.

perature, and a liquid which boiled at  $242^{\circ}$ – $247^{\circ}$ , and contained only 6.9 p.c. oxygen, instead of 11.59 as required by the same formula. By oxidation with chromic acid mixture the camphrene prepared as above yielded acetic and adipic acids—which acids are likewise obtained by oxidation of phorone from camphoric acid—together with a crystalline acid having the composition  $C^{12}H^{10}O^4$ —apparently identical with Schwanert's camphrenic acid—and exhibiting all the properties of Hofmann's insolinic acid (v. 725), of the acid which Hirzel a. Beilstein obtained by oxidation of xylic acid, and therefore having the formula  $C^8H^4(CH^3) \begin{cases} COOH \\ COOH \end{cases}$ , and of the xylidic acid of Fittig a. Laubinger.

Hence it appears probable that these several products are one and the same homologue of terephthalic acid, and that Schwanert's camphrenic acid is produced by oxidation, not of phorone, but of the hydrocarbon with which the phorone is mixed in the so-called camphrene.

Schwanert obtained from his camphrene, by the action of phosphoric anhydride, a hydrocarbon  $C^{12}H^{12}$  which boiled at  $170^{\circ}$ – $175^{\circ}$ , and was therefore regarded by him as only isomeric with cumene, which boils at  $150^{\circ}$ – $160^{\circ}$ . As, however, Schwanert's analysis of this hydrocarbon exhibits a deficiency of 1 to 1.5 p.c. in the carbon, it is probable that this hydrocarbon still contained a portion of the so-called camphrene, which would raise its boiling point.

Schwanert's camphrenic anhydride, which sublimed in white feathery crystals when camphrenic acid was heated to  $250^{\circ}$ , was perhaps benzoic acid, which, according to Hofmann, is produced, together with benzene and carbon dioxide, by distillation of insolinic acid.

**CANDLE-NUTS.**—These nuts, so called from their property of taking fire and burning with a bright flame, like ordinary candles, are the fruit of *Aleurites triloba*, Forst. (*A. Ambinua*, Pers.; *A. moluccana*, Willd; *Croton moluccanum*, Linn.); a shrub belonging to the order *Euphorbiaceæ*, tribe *Acalifæ*, indigenous in the Moluccas and in some of the islands of the Pacific. They are also known by the name of *Bancoul* nuts, and in Tahiti by that of *Tiili*.

The fruit of *Aleurites triloba* is formed of two large fleshy drupes, adhering laterally, and divided internally into two cells, each of which contains a single indehiscent seed of the size of a common nut, and is covered, especially in the furrows, with a thin whitish skin of earthy aspect, beneath which is the husk, of blackish colour, and very hard. The almond is white, and formed of a large oleaginous albumen, surrounding the homotropous embryo, which is provided with thin membranous cotyledons rather narrower than the albumen.

The seeds are usually sent to Europe deprived of their husks, which are used as fuel. The imperfect combustion of these husks serves in Tahiti for the preparation of a kind of lampblack, used by the natives in tattooing. In the same locality the bark of the shrub is used for the manufacture of various textile fabrics.

The fresh almonds have a not unpleasant taste, but are difficult to digest, and exert a purgative action even in moderate doses. In the islands of the Pacific they are eaten only after slight torrefaction, which renders them innocuous. They are, however, chiefly used by the natives for the extraction of oil for burning. The shelled almonds quickly turn rancid, acquiring a yellow-brown colour and a disagreeable taste. The fat extracted from them is subject to similar alterations. This fat is used in Europe solely for soap-making. The oil-cake forms an excellent manure.

The average weight of the husks is 6.5 grams; of the almonds, 3.3 grams.

Composition of the Husks.				Composition of the recently shelled Almonds.			
Water	.	.	3.71	Water	.	.	5.25
Organic matter	.	.	89.90	Fat (extracted by carbon sul- phide)	.	.	62.97
Mineral matter	.	.	6.39	Cellulose and other organic matters	.	.	28.90
				Mineral matter	.	.	2.79
			100.00				100.00

Nitrogen, 3.64 p.c.

*Composition of the Ash of the Almond.*

	In 100 parts of ash	In 100 parts of the almonds in their natural state
Lime . . . . .	18.69	0.52
Magnesia . . . . .	6.01	0.17
Potash . . . . .	11.33	0.31
Phosphoric anhydride . . . . .	29.30	0.82

The fatty matter extracted from the almonds by carbon sulphide at ordinary temperatures forms a transparent, amber-yellow, syrupy liquid. When cooled to  $-10^{\circ}$  it becomes viscous, but neither loses its transparency nor changes colour (Nallino, *Gazzetta chimica italiana*, ii. 257).

**CAOUTCHOUC.** The sulphur in vulcanised caoutchouc is easily oxidised by ozone. A. M. Wright (*Syll. Am. J.* [3] iv. 29) observed that the ebonite insulators belonging to Holtz's electrical machine, and the ebonite jackets of some induction-coils, became unusually hygroscopic soon after the instruments had been used for the production of ozone, to such an extent, indeed, that the accumulated liquid was sometimes so abundant as to trickle down in drops. An examination of this liquid showed that it contained a considerable amount of free sulphuric acid, the presence of which was attributed to the action of the ozone upon the sulphur of the vulcanised caoutchouc. Experiments were made which confirmed this supposition. Air, strongly ozonised, was passed through a vulcanised rubber tube, and then bubbled through water. In a short time the water acquired the odour of sulphurous acid, and ultimately gave a white precipitate with barium chloride.

In a similar manner a thin dry slip of ebonite placed in a small bottle into which ozone was driven became in a short time bedewed with moisture having an acid reaction, and exhibiting the same properties as that formed on the insulators of the machine. An attempt to oxidise free sulphur by means of ozone was unsuccessful.

The caoutchouc of Borneo yields a saccharine substance called bornesite, having the composition  $C^4H^{14}O^6$  (p. 206).

**CAPILLARITY.** *Constants of Capillarity* (G. Quincke, *Pogg. Ann.* cxxiv. 356; cxxv. 621; cxxviii. 141; cxxix. 1). The great tenacity exhibited by fused substances, like glass or cement, which, while in the fused state, have been able to form a surface of equilibrium, leads to the idea that the phenomena of capillarity are developed not only in liquids, but likewise in solid bodies, the smallest particles of these bodies being indeed not absolutely fixed, but susceptible of a certain amount of displacement. Many phenomena may, according to Quincke, be explained on the assumption of a tension existing on the surface of solid bodies, whether this surface is free, that is, bounded by the air, or the surface of separation between the body in question and another body, solid or liquid. If the free surface of a body is the same as that of a liquid acted upon by the same external forces, this free surface must possess a certain degree of tenacity measured by the tension exerted on a linear unit of the surface. The tenacity of round metallic wires may therefore be expressed by two members, the first of which is proportional to the transverse section, the second to the periphery of the wire.

The law for the tenacity of metallic wires has also been deduced empirically from numerous experiments by Karmarsch (*Dingl. polyt. J.* cliv. 45), who represents the tenacity (in half-kilograms) by the formula,

$$\tau = a D^2 + b D$$

where  $D$  is the diameter of the wire in millimeters, and  $a$  and  $b$  are constants.

Quincke replaces this equation by the following:

$$t = \alpha \cdot 2\pi r + \beta \cdot \pi r^2$$

where  $t$  is the tenacity in grams,  $r$  the radius of the wire in millimeters, and  $\alpha$ ,  $\beta$  are constants related to  $a$  and  $b$  as follows:

$$\alpha = \frac{b}{\pi} 500; \quad \beta = a \cdot \frac{1}{\pi} 500$$

The quantity  $\alpha$ , called the constant or coefficient of capillarity, denotes the weight in grams of the tension exerted on 1 mm. of the surface (periphery) of the wire; in other words, it is the measure of the surface-tension of the wire.

In liquids the same constant is the weight of the liquid column raised by capillarity in a tube of given diameter.

The following Table contains the results deduced from Karmarsch's experiments.



*Capillarity-constants,  $\alpha$  of Solid Metals.*

	Hard-drawn	Annealed
	grams	grams
Iron . . . . .	5731	1592
Platinum . . . . .	3025	2388
Copper . . . . .	2388	0
Silver . . . . .	2388	478
Gold . . . . .	1592	478
Zinc . . . . .	557	—
Steel . . . . .	6685	955
Nickel-silver . . . . .	6685	1114
Silver . . . . .	5253	2547
Gold (14 carats) . . . . .	3661	2228
Brass (wire) . . . . .	2547	1751
" (threads) . . . . .	1751	687

The order of the metals in this table is the same as that which they assume when arranged with regard to their hardness, as determined by the experiments of Calvert & Johnson (*Phil. Mag.* [4] xvii. 114).

*Capillarity-Constants of Fused Bodies.*—To determine these constants, the noble metals, in the form of thin vertical wires, and glass in the form of threads, were melted in a flame of the lowest possible temperature, till the drop hanging to the end fell down. Neglecting the small weight of the fused mass remaining attached to the thin wire or thread, the weight  $W$  of the fallen drop is the greatest weight that the fused vertical mass is capable of sustaining. The constant of capillarity  $\alpha$  of the fused metal is therefore determined by the relation,

$$W = \alpha \cdot 2\pi r$$

where  $2r$  is the diameter of the wire in millimeters.

Base metals and other bodies, as zinc, tin and selenium, were fused in glass tubes, the funnel-shaped extremities of which were inserted into narrow vertical tubes. For easily oxidizable bodies, such as phosphorus, cadmium, lead, antimony and bismuth, the drops were formed (by means of a peculiar apparatus) in an atmosphere of carbonic anhydride. Sodium and potassium were made to drop into rock-oil; the number obtained for potassium is however regarded as uncertain.

The capillarity-constants of gold, cast iron, silver and copper were determined by another method, which will be described hereafter.

The capillarity-constants of salts were estimated by fusing beads of them on a horizontal platinum wire of known diameter, and adding or removing portions of the salt by means of another thin platinum wire, till the quantity of salt was found which would just hang, or just drop, from the end of the wire when placed vertically. The falling drops were received on platinum foil and weighed, hygroscopic salts between watch-glasses.

The capillary coefficients of water, mercury and bromine were determined by the more exact method of measuring the heights of these liquids in capillary tubes. That of sulphur is calculated from the experiments of Frankenheim (*Jahresb. f. Chem.* 1847-48, 4); that of wax from the experiments of Wertheim (*Zamminer's Jahresb. f. Phys.* 1857, 5).

The mean values of the several capillarity-constants are given in the following table, the substances being arranged in the order of magnitude of these constants. The values of  $\alpha^2 = \frac{2\alpha}{\sigma}$  and of  $\alpha$  are also given,  $\sigma$  being the specific gravity of the fused body. The specific gravities  $\sigma_0$  at  $0^\circ$  were determined directly, excepting in the case marked with asterisks, and thence the specific gravities for the melting points were calculated. These calculations are, however, liable to some uncertainty, for want of exact data as to the coefficient of expansion, the melting point, and the expansion or contraction which takes place in fusion:—

*Capillarity-Constants of Fused Bodies.*

Substance	Melting point	$\sigma_0$	$\sigma$	$\alpha$	$\alpha^2$	$\alpha$
	°			m gr.	sq. mm.	mm.
Platinum . . . . .	2000	20.033	18.915	169.04	17.86	4.227
Palladium . . . . .	1950	11.4*	10.8	136.4	25.26	5.028
Gold . . . . .	1200	18.002	17.099	131.5	15.39	3.923
Cast iron . . . . .	1200	—	7.5	101.7	27.14	5.21
" (another specimen) . . . . .	—	—	7.5	96.81	25.81	5.08
Zinc (in CO <sup>2</sup> ) . . . . .	360	7.119	6.900	87.68	25.42	5.042
" (in air) . . . . .	360	7.119	6.900	82.70	24.	4.899
Silver . . . . .	1000	10.621	10.002	79.75	15.94	3.993
Cadmium (in CO <sup>2</sup> ) . . . . .	320	8.627	8.394	70.65	16.84	4.103
Tin . . . . .	230	7.267	7.144	59.85	16.75	4.094
Copper . . . . .	1090	8.95	8.2	59.2	14.44	3.8
Mercury . . . . .	-40	13.506	—	58.79	8.616	2.941
Lead (in CO <sup>2</sup> ) . . . . .	330	11.266	10.952	45.66	8.339	2.887
Bismuth (in CO <sup>2</sup> ) . . . . .	265	9.819	9.709	38.93	8.019	2.831
Potassium (in CO <sup>2</sup> ) . . . . .	58	0.865	—	37.09	85.74	8.768
Sodium (in CO <sup>2</sup> ) . . . . .	90	0.972	—	25.75	52.97	7.278
Antimony (in CO <sup>2</sup> ) . . . . .	432	6.620	6.528	24.92	7.635	2.764
Borax . . . . .	1000	2.6*	2.5	21.60	17.28	4.254
Microcosmic salt . . . . .	—	2.502	2.45	20.57	16.79	4.098
Glass . . . . .	1100	2.452	2.380	18.09	15.21	3.899
Boric anhydride . . . . .	1300	1.83*	1.75	10.69	12.22	3.495
Water . . . . .	0	1.	—	8.79	17.58	4.193
Selenium . . . . .	217	4.3*	4.2	7.180	3.419	1.849
Bromine . . . . .	-21	3.157	3.25	6.328	3.895	1.973
Sulphur . . . . .	111	2.033	1.966	4.207	4.280	2.068
Phosphorus (in CO <sup>2</sup> ) . . . . .	43	1.986	1.833	4.194	4.575	2.140
Wax . . . . .	68	0.963	—	3.40	7.061	2.657

In another series of experiments (*Pogg. Ann.* cxxxviii. 141) Quincke has determined the capillarity-constants of salts by a method which he regards as more exact, especially in the case of compounds which are liable to be decomposed by contact with flame-gases. The substance, melted in a platinum crucible, was poured on a horizontal plate of platinum or porcelain, where it usually formed a drop having its upper surface

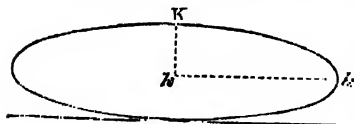


FIG. 7.

horizontal; and it is shown, by a process of mathematical analysis for which we must refer to the original paper, that the square of the vertical distance between this upper surface and the vertical element of the meridional curve of the drop ( $Kk$ , in fig. 7) is equal to the constant  $\alpha^2$  in the preceding table (called the *specific cohesion* of the liquid), which, when multiplied into half the specific gravity, gives the capillarity-constant  $\alpha$  (the superficial tension). This relation is altogether independent of the nature of the surface on which the drop is poured.

The specific gravities at the melting points were determined by the loss of weight which a platinum ball weighing 1.8 gram, fused before the oxy-hydrogen blow-pipe, sustained when thrown into water or into the fused substance; these determinations are all too small, as the temperatures were above the melting point. Under  $\sigma_0$  are given the specific gravities determined at ordinary temperatures by other observers. The numbers for certain sugars and fats are also given.

*Capillarity-Constants of Fused Bodies.*

Substance	Melting point	$\sigma_0$	$\sigma$	$\alpha$	$\alpha^2$	$a$
				m. gr.	sq. mm.	mm.
Lithium Carbonate . . . . .	—	2·111	1·787	15·64	17·39	4·17
Sodium Carbonate . . . . .	—	2·509	2·041	16·58	16·24	4·03
Potassium Carbonate . . . . .	—	2·267	2·000	14·82	14·82	3·85
Sodium Sulphate . . . . .	—	2·660	2·104	18·56	17·64	4·20
Potassium Sulphate . . . . .	—	2·660	2·100	16·73	15·92	3·99
Sodium Nitrate . . . . .	—	2·260	1·878	8·03	8·55	2·92
Potassium Nitrate . . . . .	—	2·087	1·702	7·11	8·35	2·89
Lithium Chloride . . . . .	—	1·998	1·515	6·46	8·53	2·92
Sodium Chloride . . . . .	—	2·180	1·612	6·78	8·41	2·90
Potassium Chloride . . . . .	—	1·995	1·612	7·06	8·76	2·96
Calcium Chloride . . . . .	—	2·205	2·120	10·07	9·49	3·08
Strontium Chloride . . . . .	—	2·960	2·770	11·33	8·18	2·86
Barium Chloride . . . . .	—	3·851	3·700	15·34	8·29	2·88
Silver Chloride . . . . .	—	5·550	5·300	21·68	8·18	2·86
Sodium Bromide . . . . .	—	3·079	2·448	5·00	4·08	2·02
Potassium Bromide . . . . .	—	2·415	2·199	4·93	4·49	2·12
Silver Bromide . . . . .	—	6·425	6·200	12·40	4·00	2·00
Potassium Iodide . . . . .	—	3·076	2·497	6·04	4·84	2·20
Cane Sugar . . . . .	160	1·606	1·600	6·82	8·53	2·92
Grape Sugar . . . . .	—	1·390	1·300	5·85	9·00	3·00
Pectin Sugar . . . . .	160	?	—	—	9·18	3·00
Spumaceti . . . . .	44	—	0·842	3·32	9·89	2·81
Paraffin . . . . .	64	—	0·776	3·16	8·14	2·85

The most important result deducible from this and the preceding table is that the values of the constants  $\alpha^2$  for metals and other substances may be arranged in groups of nearly equal magnitude, the numbers in which are entire multiples of 4·3. Hence it follows that when different substances in the melted state, and at temperatures a little above their respective melting points, are dropped from tubes of the same diameter, the volumes of the drops are to one another as the numbers 1, 2, 3, &c.; or more generally, that the specific cohesions of all fused bodies at temperatures near their melting points are to one another nearly as the numbers 1, 2, 3, &c.

The second table shows that fused bodies of similar chemical composition have, at temperatures near their melting points, nearly the same specific cohesion  $\alpha^2$ . Water, carbonates and sulphates (probably also phosphates), in the fused state have a specific cohesion twice as great as that of mercury; nitrates, chlorides, sugars and fats, the same; bromides and iodides half as great specific cohesion as mercury. Among the metals, lead, bismuth, and antimony have the same specific cohesion as mercury; platinum, gold, silver, cadmium, tin and copper, twice as great; zinc, iron, palladium, three times as great; sodium six times as great a specific cohesion as mercury. From experiments with borax in the oxidising blowpipe-flame, according to the first method, Quincke believes also that this body should also be included in the mercury group.

*Capillarity of Saline Solutions.*—Buliginisky (*Pogg. Ann.* cxxxiv. 440) has determined the capillarity-constants of saline solutions at different degrees of concentration, by measuring the height to which the several solutions are raised in capillary tubes at different temperatures. For the description of the apparatus used and the method of observing, we must refer to the original memoir. In the case of potassium nitrate observations on solutions of four different strengths were made in three groups: the first at temperatures varying from 9° to 12°; the second from 15° to 18°; the third from 22·5° to 24·5°. By comparison of these observations, the differences of height in the columns corresponding to the degree of temperature were determined, and by means of those differences the observed heights of the columns were reduced to the standard temperature of 15°. The mean of all the heights for each solution (for which the observed heights reduced as above deviated but little) was then calculated proportionally to the capillary height of water = 100; and by multiplying the values thus determined into the corresponding densities of the solutions, and reducing these products to water = 100, the capillarity-constants were determined, as in the following Table:—

## CAPILLARITY.

*Capillarity-Constants of Saline Solution.*

	Potassium Nitrate in 100 parts by weight of solution	Density at 15° referred to water at 4°	Mean Capillary Height	Capillarity-Constant
Distilled water . . .	—	0.99918	100.00	100.00
Solution I. . . . .	4.630	1.0270	98.00	100.73
Solution II. . . . .	7.572	1.0465	96.69	101.27
Solution III. . . . .	10.405	1.0657	95.33	101.68
Solution IV. . . . .	13.218	1.0862	93.98	102.17

If  $G$  denote the capillarity-constant of a solution,  $A$  that of distilled water;  $g$  the weight of the salt in 1 gram of the solution;  $p$  that of water in 1 gram of the solution; and  $k$  a coefficient to be determined from the observations, the connection between the observed capillarity-constants appears to be expressed with sufficient approximation by the formula:

$$G = A(p + qk.)$$

Thus for  $k = 1.1628$ , we have the following values:

calculated:	100.00	100.75	101.23	101.69	102.15
observed:	100.00	100.73	100.27	101.68	102.17

Experiments with aqueous solutions of ammonium chloride of four different strengths, made at temperatures varying from 15.0° to 16.6° gave results, from which, by calculating as above, the following values were obtained:—

	Ammonium Chloride in 100 parts by weight of solution	Density at 15° referred to water at 4°	Mean Capillary Height	Mean Temperature	Capillarity-Constant
Distilled water . . .	0	0.99918	100.00	16.0	100.00
Solution I. . . . .	5.247	1.0156	100.41	16.3	102.06
Solution II. . . . .	13.645	1.0406	100.97	16.2	105.16
Solution III. . . . .	20.449	1.0587	101.86	16.6	107.93
Solution IV. . . . .	25.242	1.0721	102.57	16.0	110.06

It is remarkable that the heights of the columns for solutions of sal-ammoniac are greater than those for water, whereas comparative experiments with solutions of sugar, sodium chloride, ammonium iodide, potassium chloride, calcium chloride, magnesium chloride, and ammonia always gave heights smaller than for water.

Calculating the capillarity-constants of the preceding sal-ammoniac solutions according to the formula  $G = A(p + qk)$  and making  $k = 1.3895$ , we find

calculated:	100.00	102.04	105.31	107.96	109.83
observed:	100.00	102.06	105.16	107.93	110.06

The relations between the capillarity and density of saline solutions have also been examined by C. A. Valson (*Compt. rend.* lxxiv. 103), whose method consists in determining the densities and the capillary heights in tubes of  $\frac{1}{2}$  mm. diameter of a series of solutions containing equivalent quantities (in grams) of the salts in a litre of water: these he calls normal solutions:—

The results are given in the following Table, in which  $E$  denotes the equivalents of the several metals;  $H$  the capillary heights of the several solutions, at the temperature of 15°;  $D$  the density of the normal solutions at the same temperature;  $DH$  the products of the capillary heights into the densities, that is to say the capillary contents:

The product of the height and density is very nearly constant, and, with two or three exceptions, lies between the numbers 61.5 and 62.0. It follows therefore that the weight of a normal saline solution raised in a capillary tube of given diameter may be regarded as constant; for a tube of  $\frac{1}{2}$  mm. diameter, this weight is 12.1 milligrams.

The numbers in the following table are also connected by the relation

$$H = 118.5 - 56.8 D,$$

which shows that in passing from one normal solution to another, the increase of capillary height is proportional to the diminution of the density.

In a previous series of experiments (*Compt. rend.* lxx. 1040) Valson examined

### *Relations between Capillarity and Density in Saline Solutions.*

[illegible]

especially the increase or decrease produced in the height of the capillary column of a normal solution by a change in one or both of the radicles contained in it, and concluded that the capillary action of each metallic and each chlorous radicle is constant and independent of that with which it is associated; and consequently that when both radicles change together, the change in the height of the capillary column is equal to the sum of the changes which would be produced by a change in each radicle separately. The change in the height of the column of a standard solution (ammonium chloride) produced by the substitution of any other radicle for the basylous or chlorous element of that solution, is called the capillary modulus of the corresponding radicle. The following table contains the moduli of a number of radicles—for a tube 5 millimeters in diameter, and for a temperature of 15°.

*Moduli of Capillarity.*

Metallic Radicle	Modulus	Chlorous Radicle	Modulus
	mm.		mm.
Ammonium, $\text{NH}^+$	0.0	Chlorides ( $\text{Cl}^-$ )	0.0
Lithium	0.05	Carbonates ( $\text{CO}_3^-$ )	0.5
Sodium	1.2	Nitrates ( $\text{NO}_3^-$ )	1.0
Magnesium	1.4	Bicarbonates ( $\text{C}^2\text{O}_6^-$ )	1.1
Calcium	1.4	Sulphates ( $\text{SO}_4^-$ )	1.2
Potassium	1.5	Sulphites ( $\text{SO}_3^-$ )	1.3
Manganese	2.5	Thiosulphates ( $\text{S}^2\text{O}_3^-$ )	1.4
Iron	2.5	Bromides ( $\text{Br}^-$ )	2.1
Zinc	2.7	Iodides ( $\text{I}^-$ )	3.9
Copper	2.9		
Strontium	2.9		
Barium	3.9		
Cadmium	4.3		
Silver	5.5		
Lead	5.9		
Thallium	7.9		

To find, by means of this table, the capillary height of the normal solution of any salt, barium nitrate for example, in a tube of the diameter above mentioned, from the known height, (60.9 mm.) of that of a normal solution of ammonium chloride, we must subtract from this height the number 4.9, that is to say, the sum of the moduli of the two radicles of barium nitrate, the result being 5.6; direct observation gives 5.9.

The chlorides of lithium and ammonium are the only salts in the above table whose capillary height is greater than that of water.

*Sphere of Action of the Molecular Forces of Capillarity* (Quincke, *Pogg. Ann.* cxxviii. 402). The phenomena of capillarity are usually ascribed to molecular forces acting only at insensible distances. Nevertheless, it appears from the experiments of several observers (*Jahresb. f. Chem.* 1861, 2; 1862, 2; *Zamminer's Jahresb. f. Physik.* 1857, 5; *Pogg. Ann.* cxix. 199), that the capillarity-constant of a given liquid varies according to the curvature of the solid wall on which the elevation of the liquid is observed. This appears to be explicable only on the supposition that the greatest distance at which the molecular forces are still effective, or in other words, the so-called radius of the sphere of action,  $l$ , is not immeasurably small. Quincke has endeavoured to determine the magnitude, or rather the lower limit of the magnitude, of this radius by the following method. A plate of glass having a clean homogeneous surface is covered with a wedge-shaped layer of another substance, the thickness of which is very small at the edge of the wedge, and then gradually increases. Now when this wedge-shaped layer is brought in contact with a liquid which does not wet it, the angle at which the last element of the surface of the liquid cuts the solid wall will depend upon the mutual attractions of the particles of the solid wall and the liquid, and will become constant only where the thickness of the wedge-shaped layer is greater than that is to say, greater than the radius of the sphere of action, since at smaller thicknesses the underlying glass plate will act upon the particles of the liquid and modify the angle. The results obtained by this method are the following:

- $l > 0.000542$  mm. for Water, Silver, Glass.
- $= 0.000483$  mm. for Mercury, Silver sulphide, Glass.
- $= 0.000059$  mm. for Mercury, Silver iodide, Glass.
- $< 0.000080$  mm. for Mercury, Collodion, Glass.

According to these determinations, the radius of the sphere of action amounts to 50 millionths of a millimeter, which is about the tenth of the breadth of a medium light-wave, or more. Quincke is further of opinion that other molecular forces, as those which determine elasticity and the optical properties of bodies, are likewise effective at finite distances: a view which, if established, would considerably modify the prevailing theoretical views respecting these forces.

*Surface-tension of Liquids, and Spreading of one Liquid on the Surface of another.*

—The following propositions relating to the surface-tension of liquids have been deduced by Plateau (*Pogg. Ann.* cxli. 44), from a comparison of the results obtained by different observers: 1. Tension exists over the whole surface of a liquid, and therefore in every liquid film. 2. This tension is independent of the curvature of the surface or film; it is of the same magnitude throughout the surface or film, and the same at each point, in all tangential directions. 3. It is independent of the thickness of the film, so long at least as this thickness is not less than twice the radius of molecular attraction. 4. It varies according to the nature of the liquid. 5. In the same liquid it varies in inverse direction to the temperature; at ordinary temperatures however, the variation is but small.

The following proposition is regarded by Plateau as established by his own experiments. The superficial layer of a liquid possesses a peculiar viscosity independent of that of the interior of the mass: in certain liquids, as water, and especially in solution of saponin, this superficial tension is much stronger than the internal; in others, on the contrary, as turpentine, oil, and alcohol, it is weaker and often much weaker than the internal viscosity. In the formation and persistence of large films the part played by cohesion is as secondary as that of the internal viscosity.

On the Surface-tension of Liquids and the Formation of Drops, see also Duclaux (*Ann. Ch. Phys.* [4] xxi. 378; *Compt. rend.* lxx. 933; *Jahresb.* 1870, 31).

On Capillary Action in the Evolution of Gases, see J. C. d'Almeida (*Compt. rend.* lviii. 533; *Jahresb.* 1869, 37).

R. Ludtgo (*Pogg. Ann.* cxxxix. 620) has endeavoured to determine by experiment the limit up to which it is allowable to regard the tension of liquid films as independent of their thickness, and secondly in what manner beyond this limit, the tension is affected by the thickness of the film. He infers: 1. That a liquid film, immediately after its formation, has a thickness less than twice the radius of the sphere of action of the molecular forces (namely of a millimeter, according to Quincke), and consequently that the tension of a film is not constant, but a function of the thickness. 2. That the tension of a film increases as its thickness decreases. This second proposition is at variation with the results obtained by Monsbrugghe (*Pogg. Ann.* cxli. 608), who found that films of various thickness exhibited equal tensions, and that in the same film the greatest tension did not occur at the thinnest parts.

Ludtgo (*Pogg. Ann.* cxxvii. 362) has also made experiments on the spreading of one liquid on the surface of another, from which the following conclusions are deduced: 1. If a drop of one liquid spreads itself out on the surface of a second, the second never diffuses itself over the surface of the first. 2. If there be two liquids whose mutual adhesion is greater than the cohesion of the less coherent of the two, a drop of the less coherent liquid will spread itself out on the surface of the other. 3. On the contrary, a drop of the more coherent liquid placed on the surface of the less coherent retains its drop-like form, and becomes covered with a thin layer of the other liquid. 4. All liquids which satisfy the preceding condition as to the force of their mutual adhesion may therefore be arranged in a series, in which each liquid spreads itself out on the surface of the following one, never the contrary. 5. This series is the same as that which is obtained when the same liquids are arranged according to their constants of capillarity, beginning with the smallest, as in the following table:—

Ethyl Oxide . . .	1.89	} Frankenheim	Glycerin . . .	4	Plateau
Ethyl Acetate . . .	2.292		Nitric acid . . .	6.026	} Frankenheim
Alcohol . . .	2.406		Sulphuric acid . . .	6.623	
Benzene . . .	2.78		Hydrochloric acid . . .	7.026	
Turpentine-oil . . .	2.78		Ammonia . . .	—	
Plateau's Soap . . .	2.8	Plateau	Cupric Sulphate . . .	—	
Acetic acid . . .	2.884	Bède	Water . . .	7.58	Frankenheim
Poppy-oil . . .	3.05	} Guthrie	Solution of Sal-ammoniac . . .	—	
Carbon Sulphide . . .	3.31		Solution of Ferric Chloride . . .	—	
Potash solution . . .	—				

6. The spreading takes place more distinctly in proportion as the two liquids are

less miscible and as the difference of their cohesion is greater. 7. The spreading of a liquid on its own surface may be produced by placing a drop raised to a higher temperature on the surface of the same liquid at a lower temperature. 8. The greater the cohesion of any liquid, the greater is the difficulty of keeping its surface clean. See also G. van der Mensbrugghe (*Pogg. Ann.* cxxviii. 323; *Jahresb.* 1869, 39).

The following propositions relating to the capillary phenomena developed at the surface of contact of two liquids are deduced from an elaborate series of experiments by Quincke (*Pogg. Ann.* cxxxix. 1-89):—1. At the common surface of two liquids, 1 and 2, a surface-tension is developed similar to that which exists at the free surface of a liquid bounded by the air. 2. The surface-tension or capillarity-constant  $\alpha_{1,2}$  at the common boundary-surface of two liquids, multiplied into the sum of the reciprocals of the principal radii of curvature at any point of that surface, gives the capillary pressure in the direction of the normal to the surface at that point. 3. The magnitude of this capillarity-constant  $\alpha_{1,2}$  cannot be directly determined from the capillarity-constants  $\alpha_1$  and  $\alpha_2$  of the free surfaces of the two liquids, but must be determined by special experiments. It may have all values between 0 and  $\alpha_1 - \alpha_2$ . If  $\alpha_{1,2} = 0$ , the liquids 1 and 2 are miscible in all proportions, and no drops or bubbles of either liquid can form within the mass of the other. For the rest,  $\alpha_{1,2}$  appears to be smaller, the more miscible the liquids are, and always less than  $\alpha_1 - \alpha_2$ . 4. If three capillary surfaces meet in the same point, the dihedral angles formed by the intersection of the three surfaces are equal to the three external angles of a triangle whose sides are proportional to the capillarity-constants of the three surfaces. 5. A liquid 3 spreads out on the common surface of two liquids 1 and 2, whenever  $\alpha_{1,2} < \alpha_{3,1} - \alpha_{2,3}$ . 6. A liquid 2 spreads out on the free surface of a liquid 1, whenever  $\alpha_{1,2} < \alpha_1 - \alpha_2$ . 7. If liquids which are miscible in all proportions, so that  $\alpha_{1,2} = 0$ , be so arranged in a series that each successive liquid is capable of spreading on the surface of that which precedes it, the series thus obtained is identical with that on which the liquids are arranged according to the magnitudes of the capillarity-constants of their free surfaces. 8. If a lenticular drop of a liquid 2 remains on the free surface of a liquid 1, without spreading out, then certainly in most cases, and probably in all, the free surface of the liquid 1 is contaminated with a thin film of a foreign liquid 3. The action of this foreign liquid film increases with its thickness up to a certain limit, which is equal to twice the radius of the sphere of action. 9. If a liquid 2 spreads in a thin film on a flat drop of a liquid 1 in air, or on a flat air-bubble in the interior of the same liquid, the vertical distance  $K-k$  (fig. 7, p. 244) between the horizontal and vertical portions of the capillary surface diminishes. The new form of the flat drops or bubbles may be calculated as soon as  $\alpha_{1,2}$  and  $\alpha_2$  are known. 10. When a liquid 3 spreads out on the surface of a flat drop of a liquid 2 within a liquid 1, all that can be predicted is that the depth  $K-k$  of the drop will diminish; the alteration of form in this case cannot always be determined by calculation. 11. The capillarity-constants of free liquid surfaces determined on flat drops or bubbles are larger than when they are calculated from the heights of the columns in fresh-drawn capillary tubes. The dihedral angle which a liquid makes with a clean glass surface is but rarely = 0. 12. When two liquids rest one above the other in a capillary tube, the weight of liquid raised above the general level depends upon the form of the free surface of the upper liquid  $v$ , and that of the contact-surface of the upper and lower liquids  $v$  and  $u$ . 13. The weight of liquid raised above the general level is never determined, as stated by Poisson, by the lower liquid alone; but in many cases when the two liquids are miscible in all proportions, it is determined by the upper liquid alone. 14. The mean height of the liquid  $v$  and  $u$  may be calculated from the values of the constants  $\alpha_v$  and  $\alpha_{v,u}$  measured as flat drops or bubbles when the dihedral angle made by the free surface and that of the contact-surface of the two liquids with the wall of the tube is known; this angle is only in a few cases equal to  $0^\circ$  or  $180^\circ$ . 15. Observations on the heights of liquid columns in capillary tubes, or on flat drops of a liquid, or on drops falling from vertical tubes into the air, are apt to give too small a value of the capillarity-constant, inasmuch as foreign bodies diffused through the air in the form of vapours condense on the curved capillary surface, and the resulting film of liquid spread out on that surface diminishes the superficial tension of the free surface. This source of error is greater at ordinary than at high temperatures, greater also in liquids with large than in those with small capillarity-constants, and explains the too small values of the capillarity-constants of certain liquids, as mercury and water found by former observers. 16. This condensation of vapours on the surface of liquids, exhibits the varying forms of lenticular water-drops on mercury and the so-called *Wasserbilder*.

The part played by capillarity in the diffusion of one liquid on the surface of another has also been studied by Du Bois-Reymond (*Pogg. Ann.* cxxxix. 262). When the free surface of a liquid A is covered with a thin layer of another liquid B—while



may either be totally different from the former, or a mixture of another substance with the liquid A, as when the vapours of certain liquids fall on the surface of certain others, or thirdly, a warmer film of the liquid A, brisk movements are often observed on the surface and in the interior of A, indicating that the superficial layer is striving, from some unknown cause, to extend in all directions the area of surface which it covers, and carrying with it centrifugally the covered liquid, wherever the two are in contact. The visible effect is, therefore, as if the covering liquid were actuated by a repulsive force tending to tear it asunder. The existence of such a force has been admitted by some observers, whereas others attribute the phenomena in question to capillarity or some similar force. Du Bois-Reymond regards these phenomena as due partly to capillarity, partly to manifestations of hitherto unknown forces, having their seat in sufficiently thin films of certain liquids. He points out that the meridian curve of a drop floating in equilibrium can have no point of contrary flexure either at its free or at its lower surface. The horizontal diameter of a drop of given small mass must therefore be greater as the angle at which its upper and lower surfaces meet is smaller. If this angle vanishes, the diameter of the drop becomes infinitely great, that is to say, the drop spreads itself out. He regards as vague and unsatisfactory the tension hypothesis, according to which the surface of a liquid is compared with a membrane tending to contract with a certain force depending on the nature of the liquid; and refers to the stationary diffusion of alcohol upon oil, observed simultaneously by himself and by Plateau, in which, notwithstanding the uniform centrifugal flow of the alcohol, the entire surface assumes a fixed form. Finally, he regards the existence of a repulsive force in thin films of certain liquids as established with a degree of probability equal to that which is attainable in the case of physical forces in general.

**CAPRIC or BUTYRIC ACID**,  $C^{10}H^{20}O_2 = C^9H^{19}.COOH$  (F. Grimm, *Ann. Ch. Pharm.* clvii. 264). This acid has been found, together with caprylic acid, in the fusel-oil of Hungarian wines. The liquid, freed by distillation from water, ethyl alcohol and amyl alcohol, was boiled with strong caustic soda, and the lower layer containing the sodium salts of the fatty acids was treated with dilute sulphuric acid, whereby a brown disagreeably smelling oil was separated. This oil was dissolved in dilute ammonia; the liquid freed from an undissolved fatty substance was precipitated by barium chloride; and the precipitate was collected on a linen cloth and pressed between filter paper. To remove the fatty substance which still adhered to it, the barium salt was decomposed by hydrochloric acid, and the fatty acids were saponified with a dilute solution of sodium carbonate. After repeating this operation twice, a mixture of fatty acids was obtained, which solidified at  $+20^\circ$ . On distillation, it began to boil at  $225^\circ$ , the temperature rising gradually to  $280^\circ$ , when a thick brown residue was left in the retort. A small portion of the distillate was precipitated in fractions by a hot concentrated solution of caustic baryta. The analysis of the different fractions showed that the acids consisted chiefly of capric acid with a little caprylic and perhaps a small quantity of ananthylic acid. The same acids were found by Fischer in crude ananthic ether, excepting that he obtained more caprylic acid.

To obtain pure capric acid, the mixture of acids was subjected to fractional distillation, and the portion boiling above  $260^\circ$  pressed between filter-paper, first at a very low, and afterwards at the common temperature.

Pure capric acid melts at  $30^\circ$  to a clear oil, which begins to solidify again at  $29.5^\circ$ , and boils with partial decomposition at  $268^\circ$ – $270^\circ$ .

**Methyl caprate**,  $C^{10}H^{19}(OH)O_2$ , was obtained by saturating a solution of the acid in methyl alcohol with dry hydrochloric acid gas. It is a colourless liquid, boiling at  $222^\circ$ – $225^\circ$ , and having a pleasant fruit-like smell. **Ethyl caprate**, which has been prepared by Fischer and Rowney, boils at  $243^\circ$ .

**Amyl caprate**,  $C^{10}H^{19}(C^5H^{11})O_2$ , prepared by acting with hydrochloric acid on a solution of the acid in amyl alcohol, is a light colourless liquid, which has only a faint smell. The small quantity obtained distilled between  $275^\circ$ – $290^\circ$  with partial decomposition. This ether is contained in large quantity in the Hungarian fusel-oil, which contains neither propyl nor butyl alcohol.

**Capric chloride**,  $C^{10}H^{19}.OCl$ , corresponding with the preceding acid, is best prepared by the action of phosphorus pentachloride on the acid. It has not however been obtained in the pure state, as it is decomposed by distillation and by contact with water. It is a heavy liquid, boiling at a temperature above  $200^\circ$ , and having a faint aromatic, not pungent odour.

The action of phosphorus pentachloride on the acid likewise gives rise to a small quantity of a white crystalline body, which is not acted upon by boiling water, by potash solution, and therefore does not appear to consist of capric anhydride (Grimm, *loc. cit.*).

The capric acid above described is doubtless identical with that which was obtained some years ago by Rowney from Scotch fusel-oil. It is probably an iso-acid.

Another modification, liquid even at low temperatures, has been prepared by Borodin (*Zeitschr. f. Chem.* vi. 416), by oxidation of the decyl alcohol  $C^{10}H^{22}O$ , which he obtained in 1864 by the action of sodium on valeral (v. 972). This alcohol, heated with a dilute mixture of potassium dichromate and sulphuric acid, is converted into capric aldehyde  $C^{10}H^{20}O$ , and capric acid, which may be separated by potash-ley, the acid alone dissolving therein; the aldehyde is also converted into the acid by further oxidation.

The capric acid precipitated from the potash-solution by hydrochloric acid may be freed from admixed lower homologues by converting into the calcium or cadmium salt, both of which are crystallisable. It boils at  $241.5^{\circ}$ , becomes a syrupy at  $-20^{\circ}$ , but does not solidify even at  $-37^{\circ}$ . It has a faint odour and a disagreeable rancid taste, is insoluble in water, but dissolves readily in alcohol and ether.

The potassium, sodium, and ammonium salts are obtained by neutralisation; the rest by precipitation. The *potassium salt*  $K(C^{10}H^{19}O_2)$  is an amorphous very soluble mass, the concentrated aqueous solution of which is decomposed by water, with formation of an acid salt. The *sodium salt*  $Na(C^{10}H^{19}O_2)$  is very much like the potassium salt. The *silver salt*  $Ag(C^{10}H^{19}O_2)$  is a white precipitate somewhat soluble in hot alcohol, from which it separates in flocks on cooling. The *cadmium salt*  $Cd(C^{10}H^{19}O_2)_2$  is also a white precipitate soluble in alcohol, from which it separates easily in needle-shaped crystals. The *calcium salt*  $Ca(C^{10}H^{19}O_2)_2$  is a white precipitate sparingly soluble in water and in alcohol, easily in ether, from which it crystallises in needles. The *strontium salt* resembles the calcium salt; the *barium salt* is oily or waxy and seldom crystallises; the *magnesium salt* is soluble. The *zinc, manganese, iron, chromium, aluminium, cobalt, nickel, copper, mercury, and lead salts* are all insoluble or slightly soluble, glutinous precipitates.

Borodin regards this modification of capric acid as an amyliated valeric acid  $C^{11}(C^{10}H^{19})_2COOH$ .

**CAPROIC ACID**,  $C^6H^{12}O_2$ .—*Normal Caproic acid*,  $(CH_2)^4CH^3.COOH$ , is prepared by heating normal amyl cyanide  $(CH_2)^4CH^3.CN$  with alcoholic potash, and decomposing the resulting potassium salt with sulphuric acid. The acid then separates as an oily layer, which may be purified by washing and distillation. It is a colourless liquid, which does not mix with water, has an odour fainter and somewhat less disagreeable than that of ordinary caproic acid, and a strongly acid taste. It boils at  $204.5^{\circ}$ – $205^{\circ}$  (bar. at 0.7385 met.); ordinary caproic acid boils at  $199.7^{\circ}$ . Its specific gravity at different temperatures is as follows:—

Temperature . . . . .	$0^{\circ}$	$20^{\circ}$	$40^{\circ}$	$99.1^{\circ}$
Specific gravity . . . . .	0.9149	0.9294	0.9172	0.8947

(Lieben a. Rossi, *Gazzetta chimica italiana*, i. 314).

The following table exhibits the composition and solubility of the calcium and barium salts of this acid, and of ordinary caproic acid prepared from fermentation amyl alcohol, by converting it into the chloride, this into the cyanide, &c. The numbers denote the quantities of *anhydrous* salt dissolved in 100 parts of water at  $185^{\circ}$ :—

	Normal	Ordinary
Calcium Salts . . . . .	$Ca(C^6H^{11}O_2)_2 + H_2O$ 2.6676–2.707 parts at $18.5^{\circ}$ ; a little more in boiling water.	$Ca(C^6H^{11}O_2)_2 + 3H_2O$ 4.4 parts at $18.5^{\circ}$ ; more soluble in hot water.
Barium Salts . . . . .	$Ba(C^6H^{11}O_2)_2$ 8.496 parts at $18.5^{\circ}$ ; much more soluble in hot water.	$Ba(C^6H^{11}O_2)_2 + 2H_2O$ 34.65 parts at $18.5^{\circ}$ ; less soluble in hot water.

The normal barium salt contained a little water, probably hygroscopic.

*Normal ethyl caproate*,  $C^6H^{13}.C^6H^{11}O_2$ , prepared by treating 10 grams of the normal acid with 10 grams alcohol of 99 p.c. and 6 grams of sulphuric acid, boils at  $166.5^{\circ}$  under a pressure of 735.8 mm., and has a sp. gr. of 0.8898 at  $0^{\circ}$ , 0.8732 at  $20^{\circ}$ , 0.8594 at  $40^{\circ}$ .

*Ordinary ethyl caproate*, prepared in like manner, boils at  $160.4^{\circ}$  (corr.) under a pressure of 737 mm. and has a sp. gr. of 0.887 at  $0^{\circ}$ , 0.8705 at  $20^{\circ}$ , 0.8568 at  $40^{\circ}$ .

The *ordinary* caproic acid, from which the preceding compounds were prepared, and a very feeble optical rotatory power: hence the statements made respecting it are not

necessarily true for every specimen of caproic acid prepared from fermentation amyl alcohol (Lieben & Rossi, *Ann. Ch. Pharm.* clxv. 118).

Normal caproic acid is contained in the less volatile portions of the crude acid obtained by the butyric fermentation of sugar. A mixture of rice, malt, milk, chopped meat and chalk, left to ferment for several weeks, yielded a mixture of acetic, butyric, and caproic acids (no propionic or valeric acid). The portion which passed over on fractional distillation between  $164^{\circ}$  and  $175^{\circ}$  consisted of butyric and caproic acids, from which the former was removed by repeated washing with water. The caproic acid which remained boiled at  $200^{\circ}$ – $205^{\circ}$ , yielded an anhydrous barium salt, 100 parts of a saturated solution of which at  $21^{\circ}$ – $22^{\circ}$  contained 8.3 parts of salt, and a calcium salt,  $\text{Ca}(\text{C}^6\text{H}^{11}\text{O}_2)^2 + \text{H}_2\text{O}$ , containing in 100 parts of solution saturated at  $21^{\circ}$ – $22^{\circ}$ , 4.4 parts of anhydrous salt (Grillone, *Ann. Ch. Pharm.* clxv. 127).

According to A. Freund (*J. p. Chem.* [2] iii. 224) ordinary caproic acid is formed, together with formic, acetic, and butyric acids (but no valeric acid), by the fermentation of wheat-bran in contact with leather-cuttings (the process recommended by Keller for the preparation of propionic acid).

This caproic acid added to a solution of cupric acetate throws down cupric caproate in bluish-green, heavy, oily drops, which after a short time become crystalline. The salt is nearly insoluble in water, and may therefore be readily obtained pure by washing; it is readily soluble in alcohol, and is obtained by spontaneous evaporation in small, dark green, anhydrous rhombohedrons (Freund).

*Zinc caproate* is formed in like manner by the action of caproic acid on zinc acetate, as a difficultly soluble crystalline precipitate, which redissolves partly on warming in the mother-liquor, and is deposited in small plates on cooling. The crystals separated from the mother-liquor are but slightly soluble in water, but readily soluble in warm alcohol, from which the salt separates in anhydrous crystalline needles having a mother-of-pearl lustre and a soapy feel. The formation of this salt may be employed as a method of distinguishing caproic acid from valeric and butyric acid, neither of which forms a precipitate when added to an aqueous solution of zinc acetate. The same salt is produced by acting on zinc oxide with an alcoholic solution of caproic acid (Freund).

**CAPRONE or DINONYL KETONE**,  $\text{C}^{10}\text{H}^{20}\text{O} = \text{CO}(\text{C}^5\text{H}^{10})^2$ , is obtained in large quantities by distilling the calcium salt of capric acid from Hungarian fusel-oil (p. 249). It crystallises in white pearly scales, which are insoluble in water, readily soluble in ether and boiling alcohol; it melts at  $58^{\circ}$ , solidifies again at  $56^{\circ}$ , and boils above  $350^{\circ}$ . It is not acted upon by a boiling mixture of 8 parts of potassium dichromate, 3 parts of sulphuric acid, and 10 parts of water; neither is it changed by dilute nitric acid; when it is heated with concentrated nitric acid, a violent action takes place, and, amongst other products, capric acid, and perhaps also caprylic acid, are formed (Grimm, *loc. cit.*).

**CAPROONE or DIAMYL KETONE**,  $\text{C}^{11}\text{H}^{22}\text{O} = \text{CO}(\text{C}^5\text{H}^{11})^2$ . E. Schmidt (*Deut. Chem. Ges. Ber.* v. 597) prepares this compound (and other ketones in like manner) by heating calcium caproate, mixed with chalk to prevent fusion, in a wide iron tube placed in a combustion furnace. After dehydration by calcium chloride and repeated fractional distillation, it has a sp. gr. of 0.822 at  $20^{\circ}$ , and boils at  $220^{\circ}$ – $221^{\circ}$  (at  $165^{\circ}$  according to Brazier & Gosleth). Nitric acid acts violently on it, forming caproic and nitrovaleric acids:



*Methyl-caproone*,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \text{C}^5\text{H}^{11} \end{smallmatrix}$ , prepared in like manner by heating a mixture of the calcium salts of caproic and acetic acids, has a sp. gr. of 0.813 at  $20^{\circ}$  (0.828 at  $0^{\circ}$  according to Popoff), and boils at  $155^{\circ}$ – $156^{\circ}$  (at  $144^{\circ}$  according to Popoff; at  $152^{\circ}$ , according to Schorlemmer's 'Lehrbuch'). With nitric acid it yields caproic and acetic acid, but no nitro-acid. With sodium bisulphite it forms an abundant crop of crystals (Schmidt).

**CAPRYL CHLORIDE**,  $\text{C}^{10}\text{H}^{19}\text{OCl}$ , see CAPRIC ACID, (p. 249).

**CARBAMATES.**—*Ammonium Carbamate*,  $\text{CO}^2\text{N}^2\text{H}^4 = \text{NH}_4^+\text{COONH}_4^-$ , splits up completely, when volatilised, into ammonia and carbon dioxide. A. Nauman (*Deut. Chem. Ges. Ber.* iv. 779), in five determinations of the vapour-density made with Hofmann's apparatus (*1st Suppl.* 1127), at temperatures ranging between  $37^{\circ}$  and  $100^{\circ}$ , obtained numbers between 0.855 and 0.891, the density calculated for  $2\text{NH}_3 + \text{CO}_2$  (4 vols.) being 0.898. The apparatus has to be heated for an hour before the tension becomes constant, and at low temperatures the tension reaches its maximum with extreme slowness, both when the point of saturation has not been previously attained, and when it has been passed over by cooling, after long continued exposure of the

substance to a higher temperature. Bodies which volatilise without decomposition, as naphthalene and carbon sesquichloride, behave differently.

From a great number of experiments, the following Table has been calculated:—

*Decomposition-Tensions of Ammonium Carbamate.*

Temp.	Tension	Temp.	Tension	Temp.	Tension	Temp.	Tension
	mm.		mm.		mm.		mm.
—15°	2·8	10°	29·8	26°	97·5	42°	278
—10	4·8	13	34	28	110	44	316
—5	7·5	14	39	30	124	46	354
0	12·4	16	46·5	32	143	48	402
2	15·7	18	53·7	34	166	50	470
4	19	20	62·4	36	191	55	600
6	22	22	72	38	219	60	770
8	25·7	24	84·8	40	248		

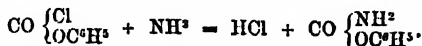
This table shows that the decomposition-tension of ammonium carbamate increases by increase of temperature similarly to the tensions of other substances.

The time required for this decomposition depends partly on the quantity of undecomposed salt present, and becomes shorter the larger the surface of the latter. Both during decomposition and during reproduction, the tension increases or decreases more slowly, the nearer it comes to the point of equilibrium.

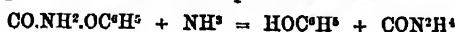
The long time required for the decomposition by heat, or for the reproduction, of this compound, shows that it is an atomic and not a molecular combination. In this respect it resembles formic metaldehyde,  $C^2H^4O^2$ , which, as Hofmann has shown, splits up when heated into three molecules of formic aldehyde  $CH^2O$ , this gas on cooling being slowly reconverted into the solid polymeric compound (Naumann, *Deut. Chem. Ges. Ber.* v. 815).

**Benzyl Carbamate**,  $CO.NH^2.OC^2H^5$ , is produced, together with benzyl chloride, by the action of cyanogen chloride, gaseous or solid, on benzyl alcohol. See BENZYL-COMPOUNDS (p. 178).

**Phenyl Carbamate**,  $CO.NH^2.OC^6H^5$ , is formed, together with ammonium chloride, by the action of dry ammonia gas on a solution of phenyl chlorocarbonate in absolute ether:

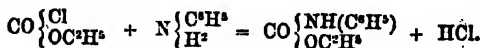


The solution filtered from the sal-ammoniac and left to evaporate, yields phenyl carbamate in beautiful laminae melting at  $141^\circ$ , soluble in alcohol and water, as well as in ether. When evaporated with strong soda-solution, it gives off a large quantity of ammonia, and forms sodium carbonate and sodium phenate. Heated to  $140^\circ$ – $150^\circ$  with saturated aqueous ammonia, it forms phenol and urea:



(Kempf, *Deut. Chem. Ges. Ber.* iii. 253).

**Ethyl Phenylcarbamate**, **Ethyllic Carbanilate**, **Phenylcarbamie Ether**, or **Phenyl-urethane**,  $C^6H^5NO^2 = CO \begin{Bmatrix} NH.C^2H^5 \\ OC^6H^5 \end{Bmatrix}$ . This ether is formed when 1 mol. ethyl chlorocarbonate is allowed to flow upon 2 mol. aniline contained in a flask connected with an inverted condenser. The whole solidifies to a crystalline mass, which, when heated in a water-bath and freed from excess of aniline by washing it, first with water containing hydrochloric acid, and then several times with cold water, yields crystals of ethyl carbanilate:



The ether may be purified either by boiling it with a large quantity of water and filtering quickly, or better, by distilling it after drying. It is nearly insoluble in cold, somewhat soluble in boiling water, easily soluble in alcohol and ether; passes over abundantly with aqueous vapour; melts at  $51^\circ$ – $52^\circ$ ; volatilises without decomposition, and boils at  $237^\circ$ – $238^\circ$ . It is decomposed by baryta-water and hydriodic acid, and carbanilic acid cannot be prepared from it. It reacts like the urethanes and appears to be only isomeric with the ethylic ether of anthranilic or meta-amidobenzoic acid (obtained by the action of boiling potash on indigo, *1st Suppl.* 751), but probably identical.

with the body which Hofmann obtained in 1849 by the action of ethyl alcohol on phenyl cyanate or carbanil (ii. 197). When treated with potash-ley, it yields at first alcohol, carbon dioxide and aniline, the last of which acts further on the undecomposed ethyl carbanilate, converting it into diphenyl-urea,  $\text{CON}^{\text{H}}\text{H}(\text{C}^6\text{H}_5)_2$ . The diphenyl-urea obtained in this manner, or directly by heating ethyl carbanilate with aniline to  $160^\circ$ , differs from Hofmann's carbanilide (i. 756) only by boiling at  $225^\circ$  instead of  $205^\circ$ , and by its smaller solubility in alcohol. Ethyl carbanilate heated with ammonia yields aniline and urea (Wilm a. Wischin, *Chem. Soc. J.* [2] vi. 192).

H. Schiff (*Deut. Chem. Ges. Ber.* vi. 649) has obtained an ethyl carbanilate differing in properties from that above described, by the action of aniline on ethyl chlorocarbonate in ethereal solution. 1 part of ethyl chlorocarbonate dissolved in 10 to 15 times its volume of absolute ether was added by drops to 2 parts of aniline; the liquid filtered from the aniline hydrochloride and evaporated; and the residue washed, first with acidulated, then with pure water, dried over calcium chloride, again dissolved in ether, and evaporated.

The product thus obtained has the composition of ethyl carbanilate, but does not crystallise. It is not volatile without decomposition, but decomposes when heated above  $200^\circ$ , giving off vapour of ether, and between  $230^\circ$  and  $235^\circ$  a colourless liquid which begins to boil in the receiver, giving off ether-vapour and an odour of phenyl cyanate, and finally solidifying to a white crystalline mass. After some time more crystals are formed, the odour of phenyl cyanate is no longer emitted, and the mass, which then contains alcohol, may be freed from the uncrystallisable portion by treatment with ether or benzene.

The crystallised mass thus obtained contains three compounds which may be separated by means of alcohol; all three, when fused with potash, yield aniline and carbonic anhydride, and when fused alone, emit the odour of phenyl cyanate. These compounds are: 1. *Triphenyl Cyanurate*,  $\text{C}^6\text{H}_5\text{N}(\text{OC}^6\text{H}_5)_3$ ; small colourless prisms, insoluble in water and in ether, nearly insoluble in cold, very slightly soluble in hot alcohol, moderately soluble in hot benzene and in the alcoholic solutions of the compounds 2 and 3. It melts at  $214^\circ$ – $216^\circ$  (corr.  $222^\circ$ ) and is identical with the compound which Hofmann obtained by heating ethyl carbanilate with phosphoric anhydride (*Deut. Chem. Ges. Ber.* iii. 765), and by the action of cyanogen chloride on potassium phenate (*ibid.* 269). 2. *Diphenyl-carbamide* or *Carbanilide*,  $\text{N}^{\text{H}}\text{CO}(\text{C}^6\text{H}_5)_2$ , identical with that obtained in various other ways (i. 756; 1st *Suppl.* 398). It forms long shining needles, melting at  $200^\circ$ – $203^\circ$ , easily soluble in hot alcohol, more soluble in cold alcohol than the preceding compound. It forms the principal part of the product obtained by the decomposition of the carbanilic ether. 3. *Triphenyl-bisret*,

$\text{N} \begin{pmatrix} \text{CONHC}^6\text{H}_5 \\ \text{C}^6\text{H}_5 \\ \text{CONHO}^{\text{H}} \end{pmatrix}$ . This constitutes the portion of the product easily soluble in alcohol;

it is best precipitated from the alcoholic solution by water, whereby an indistinctly crystalline mass is obtained which melts at  $105^\circ$ , and may be distilled but decomposes at the same time, yielding triphenyl cyanurate and diphenyl-carbamide.

Ethyl-aniline acts on ethyl chlorocarbonate less strongly than aniline, forming a compound which distils without decomposition between  $245^\circ$  and  $250^\circ$  (Schiff).

**Ethyl Tolylocarbamate or Toly-urethane**,  $\text{CO} \begin{pmatrix} \text{NH.C}^6\text{H}_4 \\ \text{OC}^6\text{H}_5 \end{pmatrix}$ , is obtained by the action of chlorocarbonic ether upon toluidine; the reaction is very violent, and is best conducted in presence of ether. The solution filtered from the toluidine hydrochloride and evaporated leaves the tolyl-urethane as an aromatic oil, which, when cooled by a freezing mixture, solidifies with difficulty. It is insoluble in water; crystallises from alcohol in long prisms melting at  $32^\circ$ . By distillation with phosphoric anhydride it yields tolyl isocyanate or tolyl-carbimide,  $\text{N} \begin{pmatrix} \text{CO} \\ \text{C}^6\text{H}_4 \end{pmatrix}$  (Hofmann, *Proc. Roy. Soc.* xix. 108).

**Ethyl Xylylocarbamate or Xylyl-urethane**,  $\text{CO} \begin{pmatrix} \text{NH.C}^6\text{H}_3 \\ \text{OC}^6\text{H}_5 \end{pmatrix}$ , obtained in like manner from chlorocarbonic ether and toluidine, crystallises in slender needles melting at  $65^\circ$  (Hofmann).

**Ethyl Naphthylcarbamate or Naphthyl-urethane**,  $\text{CO} \begin{pmatrix} \text{NH.O}^6\text{H} \\ \text{OC}^6\text{H}_5 \end{pmatrix}$ , obtained by treating naphthylamine with chlorocarbonic ether, crystallises from alcohol in needles which melt at  $79^\circ$  (Hofmann).

**CARBAZOL**,  $\text{C}^{12}\text{H}_8\text{N}$ . (Graebe a. Glaser, *Deut. Chem. Ges. Ber.* v. 12; Graebe, *ibid.* 976, also *Ann. Ch. Pharm.* cxlii. 256, cxlvii. 126).—A compound obtained in the purification of crude anthracene on the large scale, under conditions not yet precisely

specified. For purification it is distilled once or twice, then dissolved, together with an equal weight of picric acid, in tar-oil of high boiling point. The solution on cooling deposits fine red crystals of a compound of carbazol and picric acid, which when treated with ammonia, yields the carbazol. It is also produced, together with hydrogen, ammonia and ammonium cyanide, by passing aniline-vapour through a porcelain tube heated to bright redness:



and more readily by decomposition of diphenylamine,  $\text{C}^{12}\text{H}^{14}\text{N} = \text{C}^{12}\text{H}^{14}\text{N} + \text{H}^2$ . Hence it may be supposed to have the composition of imido-diphenyl

$\begin{array}{c} \text{C}^6\text{H}^5 \\ | \\ \text{C}^6\text{H}^5 \end{array} \text{NH}$ . Three determinations of its vapour-density (in sulphur-vapour) gave the numbers 5.97, 5.96 and 6.01, the calculated number for  $\text{C}^{12}\text{H}^{14}\text{N}$  being 5.85.

By sublimation or crystallisation, carbazol is obtained in beautiful white laminae or tables. It is insoluble in water, but dissolves in alcohol, ether, and benzene, sparingly at ordinary, more freely at higher temperatures. It melts at  $238^\circ$  and boils at  $338^\circ$ . It is not decomposed by passing through a red-hot tube or by distillation over red-hot zinc-dust or soda-lime. It dissolves in cold sulphuric acid, ordinary or fuming, and separates out unaltered on addition of water; but when heated to  $100^\circ$  with ordinary sulphuric acid, it is converted into carbazol-disulphonic acid. Nitric acid, according to its degree of concentration, converts carbazol into a mono- or di-nitro-compound. Fuming nitric acid acts upon it with great violence. The same nitro-derivatives are formed by the action of nitrous acid on carbazol dissolved in alcohol. Carbazol is not decomposed by hydrochloric acid, by fusion with potassium hydrate, or by heating to  $200^\circ$  with alcoholic potash-solution. Neither is it reduced by sodium-amalgam in alcoholic solution, or by hydriodic acid at  $200^\circ$ , but when heated to  $200^\circ$ – $220^\circ$  with strong hydriodic acid and amorphous phosphorus, it takes up 6 at. hydrogen and is converted into carbazoline. Carbazol is strongly attacked by oxidising agents; when dissolved in glacial acetic acid, it is readily oxidised by chromic acid, but does not yield any well-defined product. With chlorine and bromine it forms substitution-products.

The compound of carbazol with picric acid  $\text{C}^{12}\text{H}^9\text{N} \cdot \text{C}^6\text{H}_2(\text{NO}^2)_3\text{O}$  forms beautiful red needles slightly soluble in cold benzene, more freely in hot benzene and in ether. It is decomposed by water and by alcohol like the corresponding anthraceno-compound, from which indeed it is distinguishable only by the form of its crystals and by its inferior solubility in benzene. By careful heating it may be sublimed in needles, with only slight decomposition.

In the characters of its picric acid compound, as well as in not combining with mineral acids, and indeed in all the characters above described, carbazol resembles a hydrocarbon much more closely than a nitrogenised organic base.

**CARBAZOLINE**,  $\text{C}^{12}\text{H}^{14}\text{N}$ .—A base formed, as already mentioned, by the action of hydriodic acid on carbazol in presence of amorphous phosphorus. To prepare it, carbazol is heated for some hours to  $200^\circ$ – $230^\circ$  with 4 parts of hydriodic acid (b. p.  $127^\circ$ ) and  $\frac{1}{4}$  part of amorphous phosphorus; the contents of the tube when cold are mixed with water; and the solution is warmed, and filtered from a brown unctuous mass formed at the same time. The filtrate, on addition of ammonia, deposits carbazoline, which may be purified by crystallisation from alcohol.

Carbazoline crystallises from alcohol in large white needles; it melts at  $96^\circ$ , and distils at  $286^\circ$  (uncorrected); its vapour-density is 8.13, 6.99 being the calculated density for  $\text{C}^{12}\text{H}^{14}\text{N}$ . It sublimes in needles, and volatilises with water-vapour. It is readily soluble in alcohol, ether, and benzene, and forms salts with acids very soluble in water and alcohol; its hydrochloride is  $\text{C}^{12}\text{H}^{14}\text{N} \cdot \text{HCl}$ . Platonic chloride, ferric chloride, potassium dichromate, and potassium permanganate, readily oxidise its solutions, even in the cold, with formation of a brown amorphous mass; nitric acid of sp. gr. 1.2, forms a resinous body; red-hot soda-lime and melting potash are without action on it (Graebe u. Glaser, *loc. cit.*).

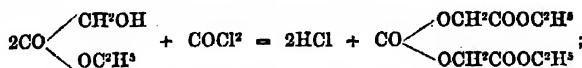
### CARBOGLYCOLLIC ETHERS (Heintz, *Ann. Ch. Pharm.* cliv. 257).

1. *Ethyl Carbodiglycollate*,  $\text{C}^6\text{H}^{10}\text{O}^2 = \text{CO} \begin{array}{l} \text{OCH}^2\text{COOC}^2\text{H}^5 \\ \text{OCH}^2\text{COOC}^2\text{H}^5 \end{array}$  is formed,

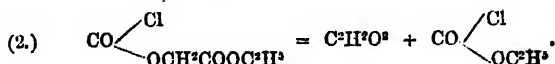
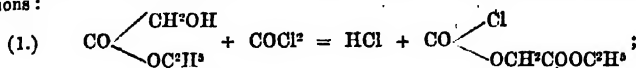
together with ethyl chlorocarbonate and glycolide, when gaseous carbonyl chloride (phosgene) is continuously passed through ethyl glycolate. On leaving the liquid to itself for some time, glycolide  $\text{C}^2\text{H}^4\text{O}^2$  separates out; and on washing this substance with ether, mixing the ethereal washings with the liquid from which the glycolide has separated, and agitating the ethereal solution with water, hydrochloric acid and ethyl

glycollate dissolve, and the remaining ethereal liquid dehydrated with calcium chloride, and evaporated, leaves a liquid which by fractional distillation yields ethyl chlorocarbonate, ethyl glycollate, and ethyl carbodiglycollate.

The formation of carbodiglycollic ether in the above reaction is represented by the equation:



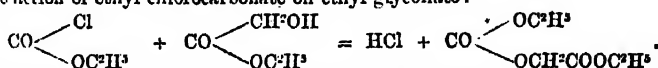
the simultaneous formation of glycollide and chlorocarbonic ether probably by the equations:



Carbodiglycollic ether is a viscid liquid of yellowish colour (probably colourless in the pure state), sinking in water, having a somewhat ethereal, not altogether pleasant odour, and a peculiar burning taste; easily soluble in alcohol and ether. It boils with partial decomposition at about  $280^\circ$ . Under the influence of bases, it decomposes, readily yielding carbonate and glycollate; probably, however, a carbodiglycollate is formed as an intermediate product, for the ether dissolves in lime- or baryta-water without immediate deposition of carbonate; but decomposition ensues on heating the liquid, and partially even when it is left to evaporate at ordinary temperatures, so that it has not yet been found possible to prepare a pure metallic carbodiglycollate.

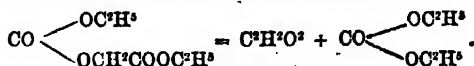
2. *Ethyl Carboglycollate*,  $\text{C}^2\text{H}^2\text{O}^3 = \text{CO} \begin{array}{l} \text{OC}^2\text{H}^3 \\ \text{OCH}^2\text{COOC}^2\text{H}^3 \end{array}$ , is produced

by the action of ethyl chlorocarbonate on ethyl glycollate:



A mixture of the two ethers is heated to  $100^\circ$  in a sealed tube till hydrochloric acid no longer escapes on opening the tube; and by subjecting the product to repeated fractional distillation, carboglycollic ether is at length obtained in the form of a somewhat viscid colourless liquid boiling at about  $240^\circ$ . It has a pleasant though faint ethereal odour, and a disagreeable burning taste; sinks in water; dissolves in alcohol and ether; also, without turbidity, in cold lime- and baryta-water. Hence metallic carboglycollates appear to be producible, but they are very easily resolved into carbonates and glycollates.

In the preparation of this ether, glycollide and ethyl carbonate are formed at the same time by a simple decomposition of the ethyl carboglycollate:



**CARBON.** *Allotropic Modifications.*—Döbereiner found, several years ago, that all kinds of carbon heated in the electric arc of a battery of 500 to 600 Bunsen's elements, soften and are ultimately converted into graphite. According to Bettendorf (*Arch. Pharm.* [2] xlv. 79), gas-coke may be thus transformed by a battery of only 24 elements. When wood (of box, ash, hornbeam, elder, lilac or cork), or flax, hemp, cotton, paper, or silk is placed in a porcelain tube, vapour of carbon sulphide passed over it at ordinary temperatures till all the air is driven out, and the tube then slowly and gradually heated to redness for about an hour, the organic substance is found, after cooling, to be converted into a kind of coke, having the ring of steel, silver, &c., and a great power of conducting heat and electricity. When heated it gradually becomes incandescent throughout its whole mass, without taking fire at any particular part, and cools down as soon as the source of heat is removed; it might, perhaps, be used to form the carbon cylinders of Bunsen's battery. It exhibits metallic lustre on its surface, is denser than wood-charcoal, and does not sensibly absorb gases. A kind of carbon, which is a good conductor of heat and electricity, and does not absorb gases, is likewise obtained by strongly heating wood in a crucible filled with charcoal powder. Wood-spirit, hydrocarbons, &c., likewise act like carbon sulphide in converting wood into elastic and conducting carbon.

time, whereby the interior of the tube becomes coated with silver white threads of carbon about a centimeter long (Sidot, *Compt. rend.* lxx. 605).

**Carbon in Meteorites.** Certain meteorites contain carbon, both in the free and in the combined state, that is, in the form of hydrocarbons; the combined carbon is completely dissolved out by free acids. In two samples of meteoric iron from Cailla, Boussingault (*Compt. rend.* lxxiv. 1287) found 0.12 p.c. combined carbon. Three specimens of meteoric iron from Orivvak, in Greenland, were found by Daubrée (*ibid.* 240) to contain:

Combined Carbon . . . .	3.00	2.6	3.6 p.c.
Free Carbon . . . . .	1.64	0.3	1.1 „

The meteorite found at Cranbourne near Melbourne contains fragments of pyrites and a certain quantity of amorphous carbon. On treating the amorphous carbon, first with nitric acid, to remove admixed pyrites, and then with a mixture of fuming nitric acid and potassium chlorate, a greenish graphitic oxide is obtained, identical in all respects with the oxide from the graphite which crystallises from molten cast-iron, but different from the oxide obtained from plumbago. From its association with pyrites in the meteorite, the carbon may have arisen from the action of carbon sulphide on the incandescent iron; at any rate, it has been formed under the influence of a very high temperature (Berthelot, *Compt. rend.* lxxiii. 494).

**Carbon from the decomposition of Carbonic Oxide by Iron.**—In the decomposition of carbonic oxide by iron and oxide of iron, at a comparatively low temperature, a large quantity of amorphous carbon is produced. By repeated treatment with nitric acid and potassium chlorate, this carbon dissolves almost completely, in the same way as the combined carbon in carburetted iron and manganese, a trace only of graphitic oxide being formed (Berthelot).

**CARBON BROMIDE (TETRA-),  $\text{CBr}_4$**  (Bolås a. Groves, *Chem. Soc. J.* [2] ix. 773). The formation of this compound by the action of bromine in presence of iodine bromide or antimonious bromide on carbon sulphide, bromopierin or bromoform, has been already noticed (1st Suppl. 400. See also Bromoform, in this volume). Subsequent experiments have shown: (1). That this compound is formed in small quantity when carbon sulphide is heated with pure bromine alone to  $180^\circ$ – $200^\circ$  for several hundred hours; (2). that the quantity produced is greatly increased by the presence of the bromides of bismuth, arsenic, gold, platinum, cadmium, zinc, or nickel, whereas the bromides of iron, tin, phosphorus and sulphur have but little influence on the result. Bismuth heated with carbon sulphide and excess of bromine for a considerable time, converts a large proportion of carbon sulphide into tetrabromide, apparently yielding a result as good as that obtained with antimony; arsenious bromide under similar circumstances also transforms the greater portion of the carbon sulphide. On the whole, however, iodine bromide in presence of excess of bromine appears to be the most convenient agent for effecting the conversion. Carbon tetrabromide is also produced in the following reactions.

**a. By decomposition of Bromopierin,  $\text{CBr}_3(\text{NO}^*)$ .** When this liquid, in quantities of 200 to 300 grams, is gently heated for thirty or forty hours in a flask connected with a condensing apparatus, nitrogen oxides and carbon dioxide are given off, a dark red liquid having nearly the composition  $\text{NOBr}$  collects in the receiver, and the liquid remaining in the flask deposits after some time large crystals of carbon tetrabromide. To obtain this compound in the pure state, the liquid is mixed with water, caustic soda added to neutralise excess of bromine, and the solution is heated till the carbon tetrabromide melts into a cake. The product thus obtained contains a small quantity of an oily substance, which may be removed by strong pressure between bibulous paper before crystallisation. Traces of bromopierin which remain undecomposed, unless the heating has been continued for a somewhat longer time than that above specified, may be removed by heating the product with aqueous potassium cyanide. The action of heat on bromopierin affords an easy and expeditious method of preparing small quantities of carbon tetrabromide, the yield being about 30 p.c. In operating on small quantities, however, care must be taken that the liquid does not dry up on the sides of the vessel, and become strongly heated, as in that case the whole is apt to decompose with explosive violence.

**b. By the action of Bromine on Iodoform,  $\text{CHI}_3$ .** At ordinary temperatures this reaction gives rise to bromoform,  $\text{CBr}_3\text{H}$ ; but an excess of bromine at high temperatures removes the whole of the iodine, producing carbon tetrabromide. When one part of iodoform was introduced into a tube, and six times its weight of bromine added to it, the mixture became white, and much iodine was liberated. The tube was then sealed and heated to about  $180^\circ$  for 70 hours, and on opening it at the expiration of that time, a considerable quantity of hydrobromic acid



escaped. The contents were then neutralised with sodium hydrate, and distilled in the usual way. The semi-solid crystalline mass, after being separated from the water, and having the greater portion of the oily matter removed by pressure, was examined, and found to be carbon tetrabromide contaminated with a minute quantity of the above-mentioned oil, which was, however, easily removed by crystallisation from spirit. In this experiment bromiodoform was undoubtedly first produced, the liberated iodine combining with the excess of bromine; and the bromide of iodine thus formed, acting upon the bromiodoform, transformed it into tetrabromide of carbon.

γ. *By the action of Iodine Bromide and Bromine on Chloroform.*—This reaction yields the compounds  $\text{CBr}^4$  and  $\text{CBr}^3\text{Cl}$ , together with other products. When dry chloroform was heated to  $150^\circ$  in sealed tubes with one part of iodine and 3 parts of bromine till the tubes on being opened no longer emitted gas, the contents when submitted to fractional distillation yielded several fractions, the lowest of which ( $100^\circ$ – $130^\circ$ ) was liquid at ordinary temperatures, while the intermediate fractions deposited large colourless crystals when cooled, and the highest ( $180^\circ$ – $200^\circ$ ) solidified at once to a crystalline mass, which when recrystallised from alcohol had nearly the composition of tribromochloromethane  $\text{CBr}^3\text{Cl}$ . Another rectification of the higher fraction yielded a substance, which, after crystallisation from spirit, melted at  $76^\circ$  and gave by analysis 92.91 p.c. bromine and 3 p.c. chlorine. Now as carbon tetrabromide contains 96.4 p.c. bromine, it would appear that the substance in question was simply carbon tetrabromide contaminated with a small quantity of tribromomethane.

*Boiling point and Specific gravity.*—The following table gives the results of two parallel series of experiments made with the tetrabromide prepared from carbon sulphide and from bromopierin. Column I. represents the pressure in millimeters; column II. the boiling point of the tetrabromide derived from carbon bisulphide; column III. the boiling point of that from bromopierin:—

I.	II.	III.
mm.	$\text{CBr}^4$ from $\text{CS}^2$ .	$\text{CBr}^4$ from $\text{ON}^2\text{Br}^2$ .
50	101.75	101.75
100	120.50	121.00
228	143.00	143.50
280	150.00	150.50
380	160.25	161.00
430	—	165.50
482	—	169.50
558	—	175.00

Tetrabromide of carbon under the ordinary pressure (760 mm.) boils at  $189.5^\circ$ , but at the same time it undergoes a slight decomposition, bromine being liberated. It can, however, be distilled without change in a vacuum, but, when the pressure is increased to about 360 mm., a very slight decomposition commences.

The specific gravity of carbon tetrabromide was found to be 3.42 at  $14^\circ$ ; but the result is perhaps rather too low, as the substance is very apt to form cavities in crystallising.

*Reactions.* 1. Carbon tetrabromide heated to  $200^\circ$  in a sealed tube, undergoes partial decomposition, a small quantity of bromine being liberated. The same phenomenon takes place when the tetrabromide is exposed to bright sunshine, the substance at the same time showing a strong tendency to crystallise on the side of the tube nearest the light, in well-formed and very brilliant crystals.

2. Carbon tetrabromide heated to  $100^\circ$  with alcohol in a sealed tube, yields hydrogen bromide, aldehyde and bromoform:



3. Heated with alcoholic ammonia to  $100^\circ$  in a sealed tube for several hours, it likewise yields bromoform, produced as above, together with a small quantity of guanidine.

4. When 1 part of carbon tetrabromide is heated with 2 parts of aniline, the mixture turns red, and in a few seconds a powerful reaction sets in, which completes itself without further application of heat, and the mixture on cooling solidifies to a crystalline mass, consisting of the hydrobromides of aniline and carbatriphenylamine or triphenylguanidine:

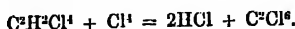


The reaction is exactly similar to that which Lehmann obtained with the tetrafluorides (i. 786), but takes place much more readily.

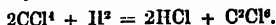
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6. The tetrachloride heated with *antimony* gives up part of its bromine, and yields a carbonaceous mass. 5. When it was heated with *silver oxalate* to  $100^{\circ}$  in a sealed tube, a violent explosion took place.

**CARBON CHLORIDES.** The trichloride  $\text{C}^2\text{Cl}^3$  is produced by the action of chlorine on acetylene tetrachloride  $\text{C}^2\text{HCl}^4$ . Acetylene tetrachloride heated in a sealed tube to  $300^{\circ}$  for fifteen hours splits up into chloroacetylene dichloride and hydrogen chloride. The action is:



Carbon trichloride is also formed, when hydrogen, mixed with the vapour of the tetrachloride, is passed through a red-hot glass tube filled with fragments of glass:



The reaction takes place at a temperature at which no perceptible resolution of the tetrachloride into the trichloride and chlorine takes place (Städeler, *Ann. Ch. Pharm. Suppl.* vii. 168).

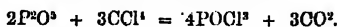
Thirdly, carbon trichloride is formed by the action of phosphorus pentachloride on acetyl chloride  $\text{CH}^3\text{COCl}$ , the oxygen-atom and the three hydrogen-atoms being replaced by equivalent quantities of chlorine. When acetyl-chloride is heated for some hours in a sealed tube to  $180^{\circ}$  with rather more than 4 mol.  $\text{PCl}^5$ , the tube being opened now and then to allow the escape of hydrochloric acid, and finally heated for 56 hours to  $210^{\circ}$ – $220^{\circ}$ , and the contents then slowly poured into cold water, carbon trichloride separates as a white mass, which may be crystallised from boiling alcohol in feathery crystals, or by slower separation in thick square plates. The crystals melt at  $182^{\circ}$ – $183^{\circ}$ , not at  $160^{\circ}$  as commonly stated (1st *Suppl.* 766).

The formation of the trichloride is accompanied by that of a small quantity of the compound  $\text{C}^2\text{H}^2\text{Cl}^3$  or  $\text{CH}^3\text{CCl}^3$  (H. Hübner u. F. C. G. Müller, *Zeitschr. f. Chem.* vi. 328).

**Tetrachloride,  $\text{CCl}^4$ .** When 1 mol. phosphorus pentoxide is heated with 2.3 mol. carbon tetrachloride to  $200^{\circ}$ – $220^{\circ}$ , the following reaction takes place:—



The quantity of phosgene produced is about three-fourths of the theoretical amount, and a portion of carbon tetrachloride always remains unchanged. By diminishing the quantity of the latter, the yield of phosgene always diminishes while that of carbon dioxide is increased. On employing equal numbers of molecules, the reaction is—



The residue in the tubes is a viscid liquid, consisting of phosphorus oxychloride, and a compound formed by the action of phosphorus oxychloride on the pentoxide (Gustavson, *Zeitschr. f. Chem.* [2] vii. 615).

Phosphorus pentasulphide has no action on carbon tetrachloride, even when the two are heated together to  $200^{\circ}$ – $220^{\circ}$  in a sealed tube for a week (Thorpe, *Chem. Soc. J.* [2] x. 453).

**Chlorobromides.** The trichlorobromide  $\text{CCl}^3\text{Br}$  is obtained by heating chloroform with bromine to  $200^{\circ}$  for six or eight hours, washing the product, and submitting it to fractional distillation. It is a mobile colourless liquid, which becomes coloured on exposure to light, has a pleasant ethereal odour, dissolves in alcohol and ether, and boils at  $104.3^{\circ}$  under a pressure of 757.9 mm. A small quantity of the dichloro-dibromide  $\text{C}^2\text{Cl}^2\text{Br}^2$ , which is a liquid boiling at a higher temperature, is likewise obtained in this reaction (Paternò, *Gazzetta chimica italiana*, i. 593).

The tetrachloro-dibromide, or tetrachloro-dibromethane  $\text{C}^2\text{Cl}^4\text{Br}^2$ , is produced, by heating pentachloroethane  $\text{C}^2\text{HCl}^5$  with bromine to  $200^{\circ}$ , as a crystalline body, which may be purified by washing with dilute potash and crystallisation from alcohol or ether, in which it is very soluble. It has a characteristic camphor-like odour, similar to that of carbon trichloride, which it closely resembles in appearance. When heated, it decomposes, with liberation of bromine, but without melting or volatilising. It has the constitution  $\begin{Bmatrix} \text{CCl}^4 \\ \text{CCl}^3\text{Br} \end{Bmatrix}$ , and is isomeric with the compound  $\begin{Bmatrix} \text{CCl}^4\text{Br} \\ \text{CCl}^3\text{Br} \end{Bmatrix}$  which Malaguti obtained (1st *Suppl.* 768), by the direct union of bromine and carbon dichloride (Paternò).

**Chloroacetylenes.** Carbon dichloride, or tetrachloroethylene  $\text{C}^2\text{Cl}^4$ , when

directly with nitrogen tetroxide, forming crystalline tetrachloro-dinitroethane  $C^2Cl^4(NO^2)^2$ . This compound is violently attacked by alcoholic potash; but if the liquid be diluted with water, and the nitro-compound gradually added to it, the formation of by-products may be avoided, and an alkaline liquid is obtained, which by evaporation yields potassium chloride, together with long prisms agreeing in

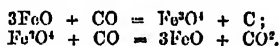
composition with the formula,  $\left. \begin{matrix} CCl^3 \\ NO^2 \\ NO^2 \end{matrix} \right\} C.O.K.$  This compound may be regarded as the

potassium salt of trichloroacetic acid in which the oxygen of the group CO is replaced by two atoms of nitryl; or as the potassium derivative of trichloro-dinitro-ethyl alcohol (Hoch u. Kolbe, *J. pr. Chem.* [2] iv. 60).

Carbon dichloride gradually added to a well-cooled mixture of concentrated sulphuric and red fuming nitric acid, forms nitryl chloride and nitrotrichloroethylene. This compound, which has not been obtained in the pure state, owing to its instability, is a yellow liquid, having an extremely intense and unpleasant odour, and causing headache and tears; it is decomposed by water and alkalis. By heating with bromine for some hours to  $140^\circ-150^\circ$  it is converted into  $C^2Cl^2(NO^2)Br^2$ , a crystalline substance, melting at about  $120^\circ$ , with decomposition (separation of bromine), easily soluble in ether, less soluble in alcohol. By heating with liquid nitrogen tetroxide in sealed tubes to  $115^\circ$ , it is converted into trinitrotrichloroethane,  $C^2Cl^3(NO^2)^3$ , which crystallises in feathery forms; this body is not explosive, but gives up nitrogen tetroxide when heated (K. Hoch, *J. pr. Chem.* [2] vi. 95).

**CARBON OXIDES.** 1. *Monoxide. Carbonic Oxide.* CO. This gas is oxidised to  $CO^2$  by chromic acid. The oxidation may be slowly but completely accomplished by introducing a ball of gypsum soaked with solution of chromic acid into carbonic oxide standing over mercury (E. Ludwig, *Ann. Ch. Pharm.* clxii. 47).

*Decomposition by Iron and its Oxides.*—When pure and dry carbonic oxide is passed over metallic iron at  $300^\circ-400^\circ$ , scarcely any deposition of carbon takes place; but when it is passed over ferrous oxide, this oxide is reduced at the surface to metallic iron and a deposit of carbon is formed. Carbonic oxide mixed with a small quantity of carbonic anhydride or oxygen, and passed over metallic iron at the same temperature, deposits pulverulent carbon on the surface of the iron. These reactions may be represented by the equations:



and

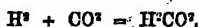
If in the experiments which yield carbon, the temperature be raised to redness, the deposition of carbon immediately stops, and any ferrous oxide that may be present is again burnt.

The carbon which is deposited in these reactions contains metallic iron, sometimes amounting to between 5 and 7 p. c., and some oxides of iron, for the most part magnetic. The presence of iron in the deposited carbon suggests the idea that natural graphite containing iron may have originated in a similar manner (Grüner, *Compt. rend.* lxxiii. 281).

*Action of Electricity on Carbon Monoxide alone and in presence of Hydrogen.*—When a mixture of hydrogen and carbon monoxide was submitted to the action of electricity in an induction tube, a contraction of the mixed gases was observed; and after the fifth hour they were found to contain about 6 p. c. of marsh-gas, which had thus been synthetically produced:



In a similar experiment, made with a mixture of hydrogen and carbon dioxide, the resultant gas was found to contain carbon monoxide, and at the same time minute drops of an oily liquid appeared in the tube. These were found to give the characteristic reactions of formic acid:



When pure and dry carbon monoxide is circulated through the induction tube, and then submitted to the action of electricity, a decomposition of the gas occurs, attended with a gradual and regular contraction, carbon dioxide being formed, whilst a transparent film of a reddish-brown colour is deposited on the sides of the tube. This film, which is entirely soluble in water, and yields a coloured solution possessing an intensely acid reaction, is an oxide of carbon, but in different experiments it does not present the same composition. Two of these 'oxycarbons,' have however been identified, namely,  $C^2O^2$ , and  $C^2O^4$ , which may be regarded as corresponding with

crotonylene,  $C^4H^4$ , and valerylene,  $C^5H^4$ , in the analogous hydrocarbon system of which acetylene is the first term (Brodie, *Proc. Roy. Soc.* xxi. 245).

**2. Dioxide or Carbonic Anhydride.**—Cailletet (*Compt. rend.* lxxv. 1271) has examined the properties of liquid carbon dioxide, which he condenses by mechanical pressure; but his experiments do not add much to the information previously furnished by those of Gore (*1st Suppl.* 402), with which he does not appear to be acquainted. It is a colourless mobile liquid, which does not conduct electricity. When the ends of the wires of a powerful induction-coil are brought near each other in this liquid, a brilliant white light is produced, unaccompanied by any deposit of carbon. It does not dissolve sodium chloride, sodium sulphate, calcium chloride, calcium carbonate, sulphur, phosphorus, stearin, or paraffin. It converts neutral sodium carbonate into acid sodium carbonate, which is insoluble in the liquid. Iodine dissolves in it sparingly, giving the tint produced by 5 milligrams of iodine in 10 c. c. of carbon bisulphide. The liquid fats are slightly soluble in liquid carbon dioxide; tallow is bleached by the abstraction of its liquid fats. Petroleum oil dissolves 5 or 6 times its volume of the liquid dioxide. It appears to be miscible with ether in all proportions. Carbon sulphide takes up a small proportion only. Liquid carbon dioxide is not reduced by sodium.

The liquid bubbles enclosed in certain minerals, as rock-crystal, topaz, amethyst and quartz appear to consist in many cases of liquid carbon dioxide, sometimes enclosing a small bubble of water. The liquefied carbon dioxide does not fill the cavities completely, and does not adhere to their sides, but moves freely about, like mercury in glass. On heating the mineral, the liquid carbon dioxide expands strongly, and condenses the enclosed water-bubble. When, however, the water predominates, the bubble does not disappear on heating (Vogelsang u. Geissler, *Pogg. Ann.* cxxxvii. 56).

Respecting the amount of carbon dioxide contained in the air near the Baltic Sea; see ATMOSPHERE (pp. 112, 113).

**Decomposition by the Electric Discharge.**—A. Thénard (*Compt. rend.* lxxiv. 1280) by passing gaseous carbon dioxide through a tube similar to those used by Houzeau for the preparation of ozone, finds that from 4 to 8 p.c. of the gas is decomposed, yielding, after absorption of the undecomposed portion by potash, a mixture of 1 vol. carbon monoxide and  $\frac{1}{2}$  vol. oxygen, 255 c.c. of which were obtained in thirty hours. Ozone was likewise formed, but its quantity was extremely small, indicating that the energy of the electric discharge was almost exclusively consumed in decomposing the carbon dioxide.

**Action of Carbon and Iron on Carbon Dioxide at a red heat.**—It has been lately asserted by Dubrunfaut (*Compt. rend.* lxxiv. 125) that carbon dioxide cannot be reduced to monoxide by ignited charcoal, unless hydrogen gas or water-vapour is present. To test the truth of this assertion, Dumas (*ibid.* lxxv. 511) has undertaken a series of very careful experiments, in which charcoal, completely deprived of hydrogen and aqueous vapour by ignition in a current of chlorine, was afterwards heated to redness in a current of dry carbon dioxide. The gas collected at four different stages of the operation exhibited the following composition:—

	I.	II.	III.	IV.
Carbon dioxide . . .	0.0	0.0	4.6	0.9
Carbon monoxide . .	99.9	188.0	95.4	90.1
Gas, non-absorbable by potash or cuprous chloride	0.1	Inappreciable traces.	Inappreciable traces.	Inappreciable traces.
	100.0	188.0	100.0	100.0

These results show that, at the commencement of the operation, a trace of gas is disengaged which is not absorbed by potash or cuprous chloride, and that this gas finally disappears. Also that, towards the termination of the experiment, carbon dioxide makes its appearance in increasing quantity, having escaped decomposition because of the deficiency of carbon. The two following points may be regarded as definitely settled by the experiments: first, that charcoal absolutely deprived of hydrogen and water by the action of chlorine, will transform carbon dioxide into monoxide; secondly, that the conversion is total when the conditions are favourable, that is to say, when there is an excess of carbon, and when the current is slow.

In order to ascertain whether metallic iron exerts a similar decomposing action upon carbon dioxide, the foregoing experiments were repeated, the tube being filled with clean iron turnings, instead of charcoal. It was found that a very slow current of

carbon dioxide passing over iron at a temperature approaching nearly to whiteness, was not entirely converted into monoxide, 30 vol. and sometimes 50 vol. p.c. escaping decomposition. The difference between the action of iron and that of carbon is explained by the fact that the iron oxide formed at first, tends to reproduce carbon dioxide by acting upon the monoxide, and thus gives rise to varying mixtures of the two gases.

*Reduction of Carbonic to Formic Acid.*—When a stream of carbon dioxide is passed continuously for several days into the porous cell of a Grove's battery, formic acid is found both in the porous cell and in the outer vessel. The quantity formed in a given time is greater with unamalgamated than with amalgamated zinc, provided a little dilute sulphuric acid be added from time to time to the liquid in the outer vessel (E. Royer, *Compt. rend.* lxx. 731).

*Estimation of Carbon dioxide in Sea-water.*—Hinly (*Chem. Soc. J.* [2] x. 455) points out that the amount of carbon dioxide in sea-water cannot be correctly determined by the ordinary gasometric method, since the gas is never completely expelled by boiling the sea-water, either in a vacuum or at 100° under the ordinary atmospheric pressure, even when a stream of pure air free from carbon dioxide is simultaneously passed through the liquid. The presence of magnesium chloride in the sea-water has doubtless an essential influence on the retention of the carbon dioxide.

The total amount of the carbon dioxide may be estimated by the use either of baryta-water or of aqueous ammonia saturated with a suitable barium salt, and an ammonium salt. The following method of conducting the estimation is very simple, free from errors that might arise from the carbon dioxide of the air, and very exact, inasmuch as it depends only upon two barium determinations:—

The precipitation of the sulphuric and carbonic acid of the sea-water is performed in a graduated litre cylinder, with a quantity of the reagent which need not be exactly known, but should be slightly in excess of that which is actually required. The liquid having been set aside, out of contact with the air, till the precipitate has completely settled down, an aliquot part,  $\frac{1}{10}$ ths for example, of the clear liquid is decanted; the barium contained in it is determined as sulphate; and from this the quantity of barium which remains dissolved in the last  $\frac{1}{10}$ th of the liquid may be determined by calculation.

The barium carbonate is then dissolved by dilute acid, the liquid is filtered, and the total quantity of barium determined as sulphate. The difference gives the quantity of barium contained in the solution as carbonate, and from this the quantity of carbon dioxide may be calculated.

To avoid loss of carbon dioxide and other gases during and after the collection of the sea-water, Hinly proposes to add the reagent below the surface of the sea; and for this he has devised an apparatus consisting of a cylinder open at both ends, and capable of being closed when sunk to the required depth. For this purpose it is provided at each end with a large stopcock, which can be closed by a powerful spring, released at the proper moment by means of an electro-magnet set in action in the usual way.

On the solubility of calcium carbonate and of bone phosphate in water containing carbonic acid, see CARBONATES and PHOSPHATES.

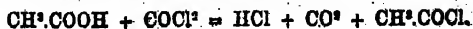
**CARBON OXYCHLORIDE,  $\text{COCl}_2$ .** *Phosgene.*—This compound is very soluble in benzene, glacial acetic acid, and most liquid hydrocarbons. It may be expelled from these liquids by boiling, but never in a state of perfect purity; for not only does the smallest trace of water contained in the solvent decompose an equivalent quantity of the oxychloride on boiling, into carbon dioxide and hydrogen chloride, but the escaping oxychloride is likewise contaminated with the vapour of the solvent.

Cold water dissolves about an equal, or at most a double volume of phosgene gas, and decomposes it very slowly, whereas alcohol decomposes it immediately, into hydrogen chloride and ethyl chloro-carbonate,  $\text{CO}.\text{Cl}.\text{OC}_2\text{H}_5$ . Aqueous potash and ammonia absorb it immediately. Very characteristic of carbon oxychloride is the fact that, when brought in contact with slightly moistened potassium bicarbonate, it triples its volume and the gas then becomes completely absorbable by water:



No other gas reacts in this manner (Berthelot, *Bull. Soc. Chim.* [2] xiii. 14).

*Action of Liquid Phosgene on Organic compounds.*—Liquid phosgene acts on acetic acid at 110°–120°, forming, acetyl chloride:

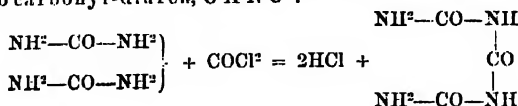


Heated to 110°–120° for some days with *acetone*, it yields a small quantity of a liquid boiling at 120°–135°, probably dichloroacetone.

When 2 parts of liquid phosgene are heated with 3 parts of *phenol* to 140°–150°, and the contents of the tube are subsequently treated with dilute soda-ley, phenyl carbonate  $(C^6H^5)_2CO^2$  is obtained, as a solid substance which crystallises from alcohol in needles. If the heating be continued for some time and the product then distilled by itself, a pungent-smelling liquid distillate is obtained, which contains phenyl chlorocarbonate  $CO.Cl.OC^6H^5$ , and when dissolved in anhydrous ether and saturated with ammonia gas, yields phenyl carbamate  $CO.NH^2.OC^6H^5$  (T. Kempf, *Deut. Chem. Ges. Ber.* iii. 632, 740).

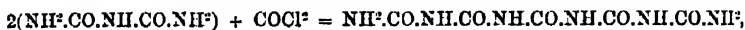
*Cresol* reacts with liquid phosgene similarly to phenol; so likewise does *thymol*, though with much greater difficulty. With *benzoic aldehyde* at 120°–130°, liquid phosgene forms chlorobenzyl chloride:  $C^6H^5.CHO + COCl^2 = CO^2 + C^6H^5.CCl^2$  (Kempf, *Zeitschr. f. Chem.* [2] vii. 77).

*Urea* heated with excess of liquid phosgene in sealed tubes to 100° for two days, is converted into carbonyl-diurea,  $C^6H^4N^2O^2$ :



By further action of the phosgene at 150°–160°, the carbonyl-diurea is converted into hydrochloric acid, and a crystalline mixture of dicyanic and tricyanic (cyanuric) acids.

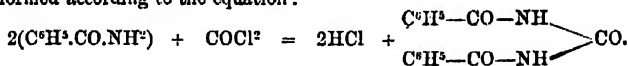
By heating *biuret* and phosgene to 60° for twelve hours, carbonyl-dibiuret  $C^6H^4N^4O^3$  is formed:



and by further action, this compound is resolved into two molecules of cyanuric acid:



*Benzamide* and liquid phosgene heated together to 160°–170° yield carbon dioxide, benzyl chloride, benzonitril and carbonyl-dibenzamide,  $C^{13}H^{12}N^2O^2$ , the latter being formed according to the equation:



With *acetamide*, in like manner, carbonyl-diacetamide,  $C^8H^8N^2O^4$ , is produced (E. Schmidt, *J. pr. Chem.* [2] v. 35; *Chem. Soc. J.* [2] x. 718).

Butlerow has shown that phosgene gas is slowly absorbed by *zinc-methyl*, forming the crystalline compound  $2Zn(CH^3)_2.C^2H^2OCl$ , which when acted upon by water yields trimethyl carbinol. He formerly stated also that a small quantity of acetic acid is formed at the same time (*1st Suppl.* 406). He now finds, however, that no acetic acid is formed by the action of water on this crystalline body; the small quantity formerly observed was probably due to the decomposition of the trimethyl carbinol (*Zeitschr. f. Chem.* [2] vi. 523).

On the action of phosgene on *anthracene* and *benzene*, see pp. 83, 131; on *glycollic ethers*, see CARBOGLYCOLLIC ETHERS, p. 254.

**CARBON OXYSULPHIDE, COS.** According to F. Salomon (*J. f. Chem.* [2] v. 476), the best mode of preparing this gas is to pass a mixture of carbon monoxide and sulphur vapour through a red-hot tube, and absorb the gas by alcoholic potash, from which it may be liberated in the pure state by hydrochloric acid.

Carbon oxy sulphide is absorbed slowly by aqueous potash, more quickly however than the vapour of the bisulphide diffused through air or any other gas. Bromine and strong sulphuric acid react with the oxy sulphide nearly in the same manner as with the bisulphide. Potassium hydrate moistened with alcohol absorbs both compounds very quickly; absolute alcohol and liquid hydrocarbons dissolve both of them in large quantity. *Ammonia* either gaseous or in solution is the best reagent for distinguishing between the two. The vapour of the bisulphide mixed with air may remain mixed with gaseous ammonia for hours without producing any distinct reaction; but when the oxy sulphide is mixed with dry ammonia gas, the sides of the vessel immediately become covered with a crystalline crust of ammonium oxy sulphide carbamate,  $NH^2.COSNH^2$ , formed by direct combination of COS and  $2NH^3$ . The

aqueous solution of this salt, heated to  $100^{\circ}$  in a sealed tube, is converted, by separation of  $\text{H}_2\text{O}$ , into ammonium sulphocyanate  $\text{CNS.NH}_4$ . The same solution gently heated with lead carbonate, gives up  $\text{H}_2\text{S}$  and yields urea  $\text{CN}^2\text{H}_4\text{O}$  (Berthelot, *Ann. Chim. Phys.* [4] xxvi. 470).

**CARBON SULPHIDES.** 1. *Bisulphide or Disulphide,  $\text{CS}_2$ .* *Preparation and Purification.* In the manufacture of this compound, the yield depends mainly on the temperature employed. Sidot (*J. Pharm.* [4] xiii. 239) by passing a known weight (40 grams) of sulphur, in the form of vapour, over 10 grams of charcoal contained in a porcelain tube heated to various temperatures, has obtained the following numbers, representing the mean results of three experiments at each of the temperatures mentioned:—

1.	At a dull red heat, 5 grams of carbon gave 17 grams of carbon bisulphide.
2.	" red heat 6.3 " " 29 " "
3.	" bright-red " 7.5 " " 19 " "

These numbers show clearly that, in order to obtain the maximum yield, a red heat should be employed, but that it should by no means be exceeded. In practice the variations in the yield of carbon bisulphide are attributed to loss, to imperfections in apparatus, and chiefly to temperature, which is always considered to be too low. The above result is due to the fact already pointed out by Berthelot, that carbon bisulphide undergoes decomposition the more completely the higher the temperature to which it is exposed. It behaves, in presence of charcoal, exactly like the carbon oxide in Deville's dissociation experiments, undergoing simple decomposition, and the liberated carbon being deposited upon the heated charcoal. Sidot has made a series of comparative experiments at different temperatures, the results of which show that decomposition takes place to some extent even at a dull red heat, but that it goes on much more rapidly at higher temperatures: 150 c.c. of carbon bisulphide were completely decomposed by passing six times over 10 grams of charcoal heated to bright redness in a porcelain tube.

To purify carbon bisulphide, Sidot first distills, and then agitates it with mercury, till it ceases to blacken the brilliant surface of the metal. This latter operation is performed as follows:—500 grams of the bisulphide, and about the same weight of mercury, are introduced into a bottle of 500 c.c. capacity, which is then agitated for some time. The sulphide formed is easily removed by filtration, and the mercury separated by means of a funnel. The two liquids are then returned to the bottle, and the agitation is renewed, until the bright surface of the mercury is no longer tarnished. Carbon bisulphide thus purified is completely free from the fetid smell which it generally possesses, and has a pure ethereal odour. It is not affected by contact with mercury for any length of time.

*Solubility in Water.*—Carbon bisulphide is not quite insoluble in water. After several days' contact at ordinary temperatures, water takes up about 1 part in 1,000 of its weight of this compound, a very small quantity at the same time undergoing decomposition. The aqueous solution when distilled gives up the carbon bisulphide unaltered, at the commencement of the distillation. It has the odour of the compound, a slightly burning taste, and does not contain more than 0.002 gram of hydrogen sulphide in a litre (Sestini, *Gazetta chimica italiana*, i. 473).

*Solubility in Alcohol.*—Carbon bisulphide does not, as usually stated, mix in all proportions, with common strong spirit, which indeed takes up less of the bisulphide in proportion as it contains more water. It is only with absolute alcohol that carbon bisulphide is miscible in all proportions. These facts afford a means of testing the strength of alcohol, as the point of saturation can be very easily determined, one drop of bisulphide in excess producing a milky turbidity. The only precaution to be attended to is to work at a temperature above  $15^{\circ}$ , because below that point the solubility decreases rapidly with the temperature, whereas above it the solubility remains nearly constant. Thus when a saturated solution is cooled down from  $+15^{\circ}$  to  $-12^{\circ}$ , about one-half of the bisulphide separates out; at  $-10^{\circ}$  one-third, and at  $+10^{\circ}$  about one-fifth.

The following results were obtained: 10 c. c. of alcohol were used in each experiment, the temperature being  $17^{\circ}$ :

*Percentage of Alcohol by weight.*

98.5 98.15 96.95 93.54 91.37 84.12 70.02 48.40 47.90

*Cub. cent. of  $\text{CS}_2$  dissolved.*

18.20 13.20 10.00 7.00 5.00 3.00 2.00 0.2 0

By inserting these values in a system of co-ordinates, a curve having the following equations is obtained:—

$$y = \frac{1}{x} \left( s - \frac{c}{x + b} \right)$$

$$x = \frac{(s - yb) + \sqrt{(s + yb)^2 + 4yc}}{2y}$$

when  $s = 1.065$ ,  $b = 0.58$ , and  $c = 0.592$ .

On calculating from these equations,  $y$ , or the quantity of bisulphide in cbc. dissolved in 10 cbc. of alcohol of  $x$  per cent. by weight, numbers are obtained agreeing almost exactly with those found by experiment. On the other hand,  $x$  can be easily calculated when we know how much bisulphide dissolves in 10 cbc. of the alcohol to be tested. Alcohol which mixes in all proportions with bisulphide may be considered as anhydrous (Tuchschmidt a. Pollenius, *Deut. Chem. Ges. Ber.* iv. 583).

**Reactions.** 1. *With the Hydrates of the Alkaline Earths.*—When a mixture of water, calcium hydrate, and carbon bisulphide is exposed to the action of solar light in summer, the liquid in six or eight hours acquires a fine yellowish-red colour, and during the following night deposits a few very fine prisms of an orange-red colour. The same reaction takes place in two hours when carbon bisulphide is heated to about  $50^\circ$  with milk of lime. The liquid filtered while hot does not deposit any crystals on cooling; but on adding calcium hydrate to the cooled filtrate, it yields the prismatic crystals above mentioned, which consist of a compound of hydrate and sulphocarbonate of calcium, represented by the formula  $3\text{CaH}^2\text{O}^2, \text{CaCS}^2 \cdot 7\text{H}^2\text{O}$ . The formation of the sulphocarbonate, which however is preceded by that of sulphide of calcium, is represented by the equation,

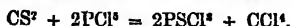


This reaction affords a test for the presence of carbon bisulphide, 0.5 c.c. of the compound is sufficient to produce it.

*Hydrate of barium* acts exactly like hydrate of calcium, and gives rise to a yellow compound which crystallises in short prisms. The hydrates of *strontium* and *magnesium* likewise act in the same manner (the latter but feebly), but do not yield crystallised compounds (Sestini, *loc. cit.*).

2. *With Lead Acetate.*—On mixing 10 c.c. of a saturated aqueous solution of carbon bisulphide (containing  $\frac{1}{10000}$  part of  $\text{CS}^2$ ) with caustic potash, heating to  $50^\circ$ , and adding acetate of lead, the liquid yields, after five minutes, a copious black precipitate of lead sulphide. The same reaction is still perceptible with a saturated aqueous solution of the bisulphide diluted with ten times its volume of water, containing, therefore, only  $\frac{1}{100000}$  part of  $\text{CS}^2$  (Sestini).

3. *With Phosphorus Pentachloride.*—According to Rathke (*Zeitschr. f. Chem.* vi. 57), this reaction yields phosphorus sulphochloride and carbon tetrachloride:



The statement of Carius (*Ann. Chem. Pharm.* cxii. 193), that carbon sulphochloride is formed in this reaction, is incorrect.

**Solid (?) Hydrated Carbon Bisulphide.**—When a strong current of dry air is passed over the surface of carbon bisulphide contained in a glass vessel, crusts of the solidified compound form, even while an immersed thermometer still stands at a few degrees above  $0^\circ$ ; the temperature, however, quickly falls to  $-17^\circ$  or  $-18^\circ$ , and white cauliflower-like masses then form on the surface, and float on the liquid; the air-delivery tube also quickly becomes stopped up by the snowy mass, and should therefore be rather wide. In a short time the whole of the liquid has disappeared, and the thermometer begins to rise, remaining constant at about  $-12^\circ$ . When a mixture of carbon bisulphide and ether (to diminish the partial pressure) is introduced into the receiver of a Carré's air-pump, it is possible, by vigorous pumping, to obtain the bisulphide in the above-mentioned cauliflower-like masses.

Solid carbon bisulphide retains its solid form for some time at ordinary temperatures, but gives off a quite peculiar aromatic odour, and is less inflammable than in the liquid state. It affords an easy means of obtaining ice of low temperature in comparatively large quantity. It is merely necessary to add to water in a glass dish a few centimeters of the liquid bisulphide, and pass a strong current of air through it, upon (if a little more of the bisulphide be used, so that this also may solidify) temperature of the whole may sink to  $-13^\circ$ . In all these experiments care must



taken to avoid the continuous inhalation of the vapour of the bisulphide (Wartha, *Deut. Chem. Ges. Ber.* iii. 80).

Berthelot, by rapid evaporation of moist carbon bisulphide, obtained a crystalline substance which he regarded as a hydrate of the bisulphide; and Duclaux afterwards assigned to it the composition  $2\text{CS}_2 \cdot \text{H}_2\text{O}$  (*1st Suppl.* 410). Ballo (*Deut. Chem. Ges. Ber.* iv. 118) regards the solid substance obtained by Wartha also as a hydrate. He put some carbon bisulphide into a shallow vessel, and directed a current of air on it, so as to strike the surface at an acute angle; with *undried* air, the formation of a snowy solid was particularly observed at the point where the current divides the liquid like a wedge, while a general formation of flakes took place in the rest of the liquid. Air, *dried* by calcium chloride, gave no formation of snow; or at most, a very slight formation. Some of the snowy substance was freed from liquid carbon bisulphide by a current of air, and the amount of water determined by Duclaux' method. Three experiments gave 17.3, 36.14, 27.09, as the percentages of water. Ballo regards the possibility of formation of ice from excess of moist air, or of loss of carbon bisulphide during the purification, as sufficient to account for the variable numbers.

To ascertain whether water is really necessary for the formation of the solid substance, he directed the air-current on the bisulphide covered with a layer of absolute alcohol, so that the air on reaching the bisulphide was thoroughly dried; in this case the snowy substance was not formed. He concludes from this that water is necessary for the production of this body, and regards it as a solidified solution of liquid carbon bisulphide in water, or of water in carbon bisulphide.

Szighelyi and Ballo (*ibid.* iv. 160) have tried the effect of a current of moist air directed on the surface of chloroform and ethyl iodide. The same formation of snow was observed, as in Ballo's experiments with carbon bisulphide; the chloroform snow was shown to contain water and chloroform by melting in a test-tube. In the case of chloroform the temperature fell to  $-13^\circ$ , in that of ethyl iodide to  $-9^\circ$ .

Wartha (*ibid.* iv. 180 and 221) regards the experiments of Ballo as inconclusive. He maintains that in his own experiments the solid bisulphide was obtained by directing a current of *dry* air on the surface of the liquid in a manner which altogether prevented the admixture of frozen atmospheric water with the solid bisulphide, and attributes the non-formation of the solid when a current of air was directed on the liquid bisulphide covered with absolute alcohol, to the fact that the temperature in this experiment fell only to  $-11.5^\circ$ , whereas the solid bisulphide melts at  $-12^\circ$  to  $-13^\circ$ .

In reply to these observations, Ballo (*ibid.* iv. 294) states that he did not observe any formation of the solid substance, even when the temperature of the above liquid was lowered to  $-18^\circ$ , which can be effected by cooling the bisulphide and alcohol with a mixture of ice and salt, and at the same time directing the air-blast on the liquid. If a layer of water be substituted for the alcohol, the formation of the hydrate of carbon bisulphide takes place at a temperature much higher than  $-18^\circ$ .

The crystalline compound was likewise formed when air saturated with vapour of carbon bisulphide was passed through a tube cooled by a freezing mixture to  $-15^\circ$ ; no crystals were obtained, however, when air dried by calcium chloride was employed.

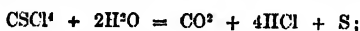
Ballo further remarks, that the solid substance obtained by Wartha by the sudden evaporation of a mixture of carbon bisulphide and ether by means of the air-pump, has not been shown to be free from water.

**2. Pentacarbon Bisulphide,  $\text{C}_5\text{S}_2$  (?).**—A substance having this composition is formed, according to L. Raale (*N. Repert. Pharm.* xix. 449), by the action of sodium on carbon bisulphide. The sodium becomes covered with a black easily separable crust which dissolves with red colour in water, and on treating the solution with chlorine or with an acid, a yellowish-brown, and afterwards a red-brown precipitate is formed. This precipitate dissolves in alkalis, ammonia, baryta-water, nitric acid, aqua regia, potassium cyanide, and sodium sulphate, but not in carbon bisulphide, alcohol, or ether. It begins to melt at  $135^\circ$ , and if then left to cool, forms an amorphous, nearly black, resinous, brittle mass, translucent with red colour on the edges. At  $150^\circ$  it decomposes, emitting extremely fetid yellow vapours. It gave by analysis 47.73 p.c. carbon and 62.27 sulphur, the formula  $\text{C}_5\text{S}_2$  requiring 48.38 and 61.62.

**CARBON SULPHOBROMIDE,  $\text{CSBr}_2$ ,** appears to be formed as an intermediate product in the preparation of carbon tetrabromide by the action of bromine and bromide of iodine on carbon bisulphide (p. 258). On pouring the product of this reaction into water, removing the iodine and excess of bromine by cautious addition of dilute soda-solution, taking care that the liquid never became alkaline (otherwise nothing but tetrabromide would have been obtained), a slightly-coloured heavy oil separated, which, when dried by calcium chloride and submitted to fractional distilla-

tion, passed over for the most part between  $150^{\circ}$  and  $160^{\circ}$ , though with considerable decomposition. The portion boiling at  $165^{\circ}$  gave 7.81 p. c. sulphur, whereas the formula  $\text{CSBr}_2$  requires 15.69 p. c.; hence it would appear that the oily liquid consisted of carbon sulphobromide mixed with the tetrabromide. The sulphobromide smells like the corresponding sulphochloride. Heated with excess of soda-solution, it is completely converted into the tetrabromide (Bolas & Groves, *Chem. Soc. J.* [2] x. 78).

**CARBON SULPHOCHLORIDES.**—*Sulphocarbonyl chloride*,  $\text{CSCI}_2$ , the analogue of phosgene, was discovered by Kolbe, who obtained it by the action of dry chlorine on carbon bisulphide (1st Suppl. 777). Another sulphochloride  $\text{CSCI}_4$ , which may be regarded as perchloromethyl-mercaptan  $\text{CCl}_3\text{SCI}$ , is formed, together with trichloromethyl-sulphurous chloride  $\text{CCl}_3\text{SO}_2$  (v. 559), by the action of moist chlorine on carbon bisulphide, or by digesting the bisulphide for several days with a mixture of manganese dioxide and hydrochloric acid; the action may be considerably assisted by addition of a little iodine; it is then completed in a week. On distilling the product, a yellow oil passes over, partly with the aqueous vapour, and afterwards trichloromethyl-sulphurous chloride solidifies in the receiver. The oil dried with lime and submitted to fractional distillation, yields, below  $80^{\circ}$ , carbon bisulphide, carbon tetrachloride, and a small quantity of sulphocarbonyl chloride, and between  $80^{\circ}$  and  $140^{\circ}$  a mixture of the preceding products with an oil the greater part of which distils between  $140^{\circ}$  and  $150^{\circ}$ ; and from this by further fractionation, perchloromethyl-mercaptan  $\text{CCl}_3\text{S}$ , boiling at  $147^{\circ}$  (corr.) may be isolated. This compound has a golden yellow colour, and a pungent, tear-exciting odour like that of sulphocarbonyl chloride. In moist air, and more quickly by heating with water, it is decomposed in the manner represented by the equation:



similarly by aqueous potash or ammonia; in the latter case ammonium sulphocyanate is likewise formed, together with a small quantity of a compound not yet examined, containing sulphur and nitrogen. When left for two or three weeks in contact with nitric acid (sp. gr. 1.2) it is converted into trichloromethyl-sulphurous chloride. Solution of potassium iodide acts upon it even in the cold, with evolution of gas, separation of iodine, and formation of hydriodic acid and a yellow glutinous solid body. Heated to  $200^{\circ}$  it is resolved into carbon tetrachloride, together with small quantities of sulphocarbonyl chloride and sulphur chloride (Rathko, *Deut. Chem. Ges. Ber.* iii. 858).

**CARBONATES.** *Ammonium Carbonates* (Divers, *Chem. Soc. J.* [2] viii. 171). There are three, if not four, true carbonates of ammonium: the normal or diammoniac carbonate, the acid or monammoniac carbonate, the half-acid ammonium carbonate, and probably a hyper-acid carbonate which Rose obtained crystallised from aqueous solution.

The normal carbonate appears to have been obtained by Dalton, but his account of it is imperfect, and has been either ignored or discredited by other chemists. Its production in the solid state presents no difficulty. It may be prepared in large crystals by adding ammonia to a warm concentrated solution of the ordinary carbonate, provided that an excess be added and not merely the calculated quantity as directed by Dalton—the presence of the ammonia serving to diminish very considerably its solubility. Another method of preparing it, also in large crystals, is to warm some water repeatedly with fresh quantities of the ordinary carbonate, and allow the solution to cool and crystallise between the additions of the carbonate, until the cold mother-liquor from the last crop of crystals, on further standing, forms crystals of the normal carbonate. In this process the first crops of crystals consist of acid carbonate, and the later ones of the half-acid carbonate. The cold mother-liquor yielding the normal carbonate on standing has been ascertained to be a solution of carbamate; and this gradually becomes converted into the carbonate. The normal carbonate can also be obtained in several other ways.

It forms elongated plates or flattened prisms, which decompose very rapidly on exposure to ammonia, water, and the acid carbonate. Its composition is expressed by the formula  $\text{CO}_2(\text{OH})^2(\text{NH}_4)^2 = \text{CO}_2(\text{NH}_4)^2\text{OH}^2$  or  $\text{CO}_2(\text{NH}_4)^2\text{H}^2$ . It is freely soluble in water, insoluble in alcohol, and only sparingly soluble in ammonia-water. Digested for some time in the most concentrated solution of ammonia at a temperature of  $20^{\circ}$ – $25^{\circ}$  in a closed vessel, it is gradually dissolved and converted into ammonium carbamate, which separates in brilliant crystals when the solution is allowed to cool.

The half-acid carbonate contains only four atoms of water instead of six, as hitherto supposed, its formula being  $(\text{CO}_2)(\text{OH})^2(\text{NH}_4) = \text{CO}_2(\text{NH}_4)(\text{OH})^2$  or  $(\text{CO}_2)(\text{OH})^2(\text{NH}_4)^1$ . A new and advantageous method of preparing it is the one already described of dissolving at a gentle heat successive quantities of the

carbonate in the same quantity of water until the crops of crystals obtained cease to consist of the acid carbonate. There are also other new ways of obtaining it.

There are several reasons for supposing that the formula of the acid carbonate ought to be  $(\text{CO}_2)(\text{OH})^2(\text{NH})^2$  instead of the half of this—the formula usually given to it. The relations of the three carbonates are exhibited in the following table:—

Normal carbonate	.	.	.	.	.	$(\text{CO}_2)(\text{OH})^2(\text{NH})^2$
Half-acid "	.	.	.	.	.	$(\text{CO}_2)(\text{OH})(\text{NH})$
Acid "	.	.	.	.	.	$(\text{CO}_2)(\text{OH})^2(\text{NH})^2$

Rose's hyper-acid carbonate probably forms the fourth member of this series.

A normal orthocarbonate,  $\text{CO}(\text{NH})^2$ , appears to exist; for the commercial carbonate mother-liquor which has just deposited the half-acid carbonate, contains more than 2 mols. of ammonia to one of carbon dioxide, and must therefore, in all probability, be a solution of the half-acid (meta) carbonate and the normal orthocarbonate.

When any of the true ammonium carbonates or the commercial carbonate are distilled, not too slowly, the principal product is the substance  $(\text{CO}_2)(\text{OH})(\text{NH})^2$  identical with the carbonate now occurring in commerce. When first obtained it is always moist from adhering water. In a day or two this moisture becomes combined with the carbamate of the salt, and often before doing so it serves to fix a little ammonia upon the acid carbonate of the salt. The per-centage numbers given by analysis, and certain of its reactions, place beyond doubt the correctness of the above formula for the commercial carbonate, although it contains 1 p. c. or so of water in excess, and often also a very little ammonia from the cause just stated. Besides the fact, that a body of this composition is formed under a variety of conditions, there is another serving to establish that the commercial carbonate is a single substance. This is that acid potassium carbonate appears to combine with ammonium carbamate and form a compound analogous to the commercial carbonate of ammonia.

When sal-ammoniac and chalk are distilled together, the products are not those stated in the text-books, namely, ammonia, water, and the carbonate of commerce, but water and ammonium carbamate. The production of the commercial carbonate occurs during the re-distillation of the crude cake. E.D.

*Calcium Carbonate.*—Experiments on the dimorphism of this compound have been made by H. Credner (*Jahrbuch f. Mineralogie*, 1871, 288), from which the following results are deduced:—

1. From a pure and cold solution of calcium bicarbonate, when saturated or moderately dilute, the normal carbonate separates at ordinary temperatures as calcspar, in the form of the fundamental rhombohedron; from more dilute solutions as prismatic aragonite.

2. The calcspar deposited from a cold solution of bicarbonate to which potassium silicate has been added, is remarkably transparent, well defined, and exhibits numerous faces. Credner had previously noticed that it is from association with apophyllite that certain calcspars of Andreasberg and Lake Superior derive their complex form. Similar results are obtained when sodium silicate or a mixture of the two silicates is used.

3. From a cold solution of the carbonates of calcium and strontium in carbonated water, the two being dissolved together, acicular or prismatic aragonite separates, even when the solution is moderately dilute. Calcium bicarbonate, to which strontium bicarbonate has been added, or introduced by dialysis, gives acicular and wedge-shaped aragonite, accompanied with crystals of calcspar, the latter increasing in number as the admixture of strontium is reduced. The spectroscopic shows the presence of a trace of strontium in the aragonite; in short, such results place it almost beyond doubt that a trifling proportion of strontium is of influence in the formation of aragonite.

4. The addition of a solution of gypsum to cold bicarbonate disposes a portion of the latter to take the form of aragonite.

5. In presence of a sufficient quantity of lead salt, calcium carbonate crystallises in the form of aragonite. This is seen in nature in the case of tarnovicite. If, however, the amount of lead carbonate present is small, the calcium carbonate separates as calcspar, with greater numbers of faces.

The general conclusions deducible from these observations are:—I. The addition of certain bodies to a solution of a mineral substance exerts an influence on the form and the number of faces of a crystal deposited from it. II. By the presence of certain bodies in its solution, one and the same mineral substance may receive an impulse to form totally different mineral species. III. Calcium carbonate, which separates from cold, pure, and not too dilute solutions of the acid carbonate, as calcspar, is deposited partly in the form of aragonite, on the addition of trifling quantities of lead carbonate, calcium sulphate, or strontium carbonate. IV. Differences in temperature and degree

of concentration of solution are not the only causes of the dimorphism of calcium carbonate.

**Hydrated Calcium Carbonate**,  $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ . — Crystals of this hydrate, which Pelouze obtained from a solution of lime in sugar-water, and Salm-Horstmar observed in a water-pipe (1st Suppl. 781), have also been found attached to conifers in a pond. This hydrate is distinguished by losing its water at temperatures above  $15^\circ$  even when immersed in water (Rammelsberg, *Deut. Chem. Ges. Ber.* iv. 469).

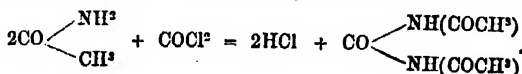
On the solubility of Calcium Carbonate in Carbonic acid water, see Schloosing (*Compt. rend.* lxxiv. 1152; *Chem. Soc. J.* [2] x. 788).

**Sodium Carbonate**. — Efflorescences, called by the natives *Coilpa* (pronounced *Koichpa*), are deposited in dry places in the bed of the Rio de Hualfin (Argentine province Chlamarea) which flows from the Sierra de Galampaja, especially in winter when the stream is slow; they are used by the natives for washing and for making soap. A specimen which had been kept for four years in a corked bottle, gave by analysis 21.475 p.c.  $\text{H}_2\text{O}$ , 24.142  $\text{CO}_2$ , 25.985  $\text{Na}_2\text{O}$ , 0.538  $\text{K}_2\text{O}$ , 6.307  $\text{NaCl}$ , 1.924  $\text{SO}_3$ , 5.788 clay and sand, and 0.554 organic matter, with traces of magnesia and lime, numbers which, neglecting the sodium chloride and other extraneous matters, lead to the formula  $\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$ . A recent specimen, on the other hand, gave 31.934 p.c.  $\text{H}_2\text{O}$ , 23.939  $\text{CO}_2$ , 34.647  $\text{Na}_2\text{O}$ , 3.484  $\text{NaCl}$ , 0.845  $\text{SO}_3$ , 0.264  $\text{MgO}$ , 4.492 clay and sand, and 0.089 organic substance, leading to the formula  $\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$  (Schickendanz, *Ann. Ch. Pharm.* clv. 359).

**CARBONYL CHLOROPLATINITE**. See PLATINUM COMPOUNDS.

**CARBONYL-DIACETIMIDE**,  $\text{C}^6\text{H}^2\text{N}^2\text{O}^3$  =  $\text{CO} \begin{cases} \text{NH}(\text{COCH}^3) \\ \text{NH}(\text{COCH}^3) \end{cases}$ , is formed

by heating acetamide to  $50^\circ$  with liquid carbonyl-chloride.



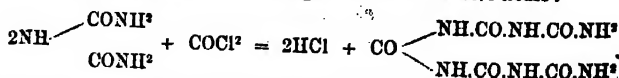
It crystallises in rhombic needles; water and alcohol dissolve it, but slowly in the cold, freely at a higher temperature. It melts when heated and sublimes without decomposition. By boiling with concentrated acids it is decomposed into ammonia and acetic acid, and when boiled for a long time with potash-solution it yields carbon dioxide and acetamide (E. Schmidt, *J. pr. Chem.* [2] v. 35).

**CARBONYL-DIBENZAMIDE**,  $\text{C}^{13}\text{H}^{12}\text{N}^2\text{O}^3$  =  $\text{CO} \begin{cases} \text{NH}(\text{COC}^6\text{H}^5) \\ \text{NH}(\text{COC}^6\text{H}^5) \end{cases}$ , is

formed in like manner when phosgene and benzamide are heated together to  $160^\circ$ – $170^\circ$ . It is sparingly soluble in water, more freely in alcohol, and crystallises in fine silky needles. With concentrated acids and with alkalis, at the boiling heat, it reacts like carbonyl-diacetamide (Schmidt).

**CARBONYL-DIBIURET**,  $\text{C}^8\text{H}^6\text{N}^6\text{O}^3$  =  $\text{CO} \begin{cases} \text{NH.CO.NH.CO.NH}^2 \\ \text{NH.CO.NH.CO.NH}^2 \end{cases}$ , is

formed by heating biuret with liquid phosgene to  $60^\circ$  for twelve hours:

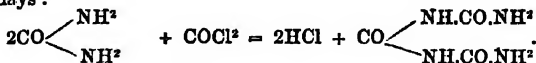


Carbonyl-dibiuret is a light, white crystalline powder, which is a little more soluble in water than carbonyl-urea, but almost insoluble in alcohol. It is soluble in alkalis and strong acids. When heated on platinum-foil it decomposes into carbon dioxide, ammonia, and cyanic acid, and when it is slowly heated in a small flask, ammonia and carbon dioxide are given off, and a residue containing urea, cyanuric acid, and ammelide is left behind.

On passing nitrous acid through a warm solution containing an excess of carbonyl-dibiuret, carbon dioxide is evolved, and as the liquid cools, urea nitrate crystallises out, mixed with a little cyanuric acid and ammonium nitrate. On boiling it with concentrated hydrochloric acid or potash-solution it decomposes into ammonia, carbon dioxide, and cyanuric acid, whilst when boiled with baryta water, it yields carbon dioxide, cyanuric acid, and urea. Like carbonyl-urea it combines only with metallic oxide; the compound  $\text{C}^8\text{H}^6\text{N}^6\text{O}^3 \cdot 3\text{HgO}$  is a white bulky powder.

By the further action of phosgene upon carbonyl-diuret, it is resolved into two mols. of cyanuric acid:  $C^3H^4N^4O^3 + COCl^2 = 2HCl + 2C^3H^2N^4O^3$ . (Schmidt).

**CARBONYL-UREA**, or **CARBONYL-DICARBAMIDE**,  $C^3H^4N^4O = NH.CO.NH^2$ , is obtained by heating urea with excess of liquid phosgene to 100° for two days:



It is a bulky white powder composed of microscopic needles, very slightly soluble in cold, more freely in boiling water, almost insoluble in cold alcohol. Heated on platinum-foil, it is resolved into ammonia and cyanic acid. When heated slowly in a test-tube, it yields ammonia and cyanuric acid. It is soluble in concentrated acids, but does not combine with them. Neither does it form compounds with salts or bases, with the exception of mercuric oxide. The compound  $C^3H^4N^4O^3.HgO$  is obtained as a crystalline precipitate, which is insoluble in water, and decomposed by dilute acids.

Carbonyl-urea is further acted upon by phosgene when the two substances are heated up to 150°-160°, hydrochloric acid being formed, together with a crystalline body, which is a mixture of dicyanic and tricyanic (cyanuric) acids (Schmidt).

**CARBOTHIALDINE**,  $C^3H^4N^4S^2$ .—This compound was obtained by Liebig & Redtenbacher by the action of carbon bisulphide on aldehyde-ammonia (1st Suppl. 802). It cannot be crystallised from water or alcohol, but is deposited in magnificent crystals from solution in concentrated aqueous ammonia. It is decomposed by iodine, nitrous acid, and mercuric chloride, yielding aldehyde, carbon bisulphide, ammonia and ammonium sulphocyanate. When 1 mol. mercuric chloride is heated with 1 mol. carbothialdine in aqueous or alcoholic solution, the whole of the mercury is quickly precipitated as sulphide, while aldehyde, sal-ammoniac, hydrochloric acid and sulphocyanic acid are produced. But when a large excess of mercuric chloride is used, a white precipitate is formed which becomes crystalline on boiling, without the production of a trace of aldehyde.

**CARBOXAMIDO BENZOIC ACID**. See BENZOIC ACID (p. 166).

**CARMINE**. See COCHINEAL.

**CARNINE**,  $C^3H^4N^4O^3$ . Weidel (*Ann. Ch. Pharm.* clviii. 353).—A base obtained from extract of meat, of which it constitutes about 1 p.c. To prepare it, the extract is dissolved in 6 or 7 parts of warm water, and carefully precipitated with strong baryta-solution, avoiding excess: the mass is filtered through a linen cloth, and the filtrate precipitated by basic lead acetate. A lead-compound of carmine is thus thrown down, and being soluble in boiling water, can thus be separated from the other bodies likewise precipitated. The aqueous solution thus obtained is decomposed while boiling with hydrogen sulphide, and the filtrate from the lead sulphide is evaporated to a small bulk and separated from a crystalline mud, sometimes deposited on standing, and due to the presence of variable quantities of sodium chloride in the extract employed, whereby ultimately more or less hydrochloric acid is formed in the crude carmine solution: the liquid portion is precipitated by strong solution of silver nitrate; and from the mixed silver chloride and silver-compound of carmine thus produced, the former is dissolved out by diluted ammonia-solution, the latter being almost insoluble in that medium: finally, the silver compound is washed with boiling water, decomposed by hydrogen sulphide, and the filtrate decolorised with animal charcoal, a considerable portion of carmine being, however, absorbed by the charcoal. From the colourless aqueous solution thus obtained, carmine crystallises on cooling in chalk-white druses and friable groups of extremely small irregular crystals, containing 1 mol. water ( $C^3H^4N^4O^3.H^2O$ ) which is given off at 100°.

The hydrochloride  $C^3H^4N^4O^3.HCl$  is obtained in needles on cooling the hot solution of carmine in strong hydrochloric acid; these needles, freed from the mother-liquor and redissolved, do not again make their appearance, a mud separating, which, however, on standing, again becomes perfectly converted into needles; the salt is anhydrous. The platinochloride has the composition  $2(C^3H^4N^4O^3.HCl).PtCl^4$ .

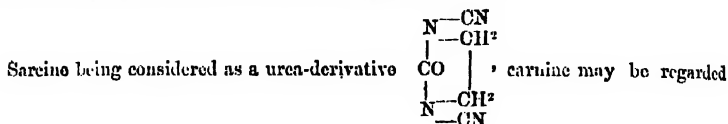
Silver nitrate throws down from a carmine solution a flocculent white precipitate, which is insoluble in nitric acid and in ammonia, and when dried at 100° has the composition  $2C^3H^4N^4O^3.AgNO^3$ ; theobromine, which differs from carmine by only one oxygen-atom, does not yield an analogous body, its silver compound being  $C^3H^4N^4O^3.AgNO^3$ ; sarcosine, on the other hand, yields the compound  $C^3H^4N^4O^3.AgNO^3$ .

Concentrated hydriodic acid does not reduce carmine to theobromine; neither does

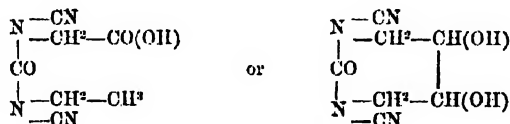
long boiling with baryta-water produce any change (no ammonia or methylamine is evolved, and unaltered carnine is found after precipitating the baryta with carbonic acid).

With bromine-water in slight excess on the water-bath, carnine gives a slight evolution of gas; after evaporation, crystals of the hydrobromide of sarcine separate, from which alkalis precipitate the base itself, soluble in excess, but nearly insoluble in cold water. From analyses of the base and its hydrobromide, and from its properties, it appears to be identical with Strecker's sarcine (v. 196), the only observed difference being that, whereas Strecker states that his sarcine is not precipitated by basic lead acetate, the base obtained as above is precipitable by basic lead acetate, though not by neutral lead acetate, or even by the basic lead salt in presence of the neutral salt. Strecker's statement is, however, in contradiction to the fact that Städeler also has prepared sarcine from the basic lead precipitate from flesh, liver, &c.

Ordinary nitric acid, heated with carnine, gives rise to a violent action, from the product of which the nitrate of sarcine is obtained on cooling: oxalic acid and an indistinctly crystalline yellow body are also produced.



as either



and the production of sarcine from carnine by bromine appears to be in accordance with the equation



Bromacetic acid might possibly be formed at the same time; but this body was not distinguishable in the ethereal extract obtained with the product of the action of bromine.

When sarcine is heated with fresh chlorine-water and a trace of nitric acid, and the solution is evaporated on the water-bath to dryness, and placed in an ammoniacal atmosphere, a dark rose-red tint is produced; carnine gives the same reaction, sarcine being previously formed.

The barium precipitate obtained in the method of extracting carnine from meat-extract, as above described, is principally phosphate and sulphate; the portion of the lead precipitate insoluble in water contains inositol, a little lactic acid, and some succinic acid; and especially an amorphous extractive matter, part of which only is soluble in alcohol. The filtrate from the original lead precipitate yields, when evaporated, a crystalline lead lactate, and the filtrate from this, when evaporated, yields much creatine with a little creatinine, the mother-liquor of which contains considerable quantities of glutinous and dextrin-like substances.

Doses of  $\frac{1}{2}$  to 2 decigrams of carnine and its hydrochloride appear to have a slight effect on the nervous system, a slackening of pulsation being the most marked symptom.

**CARVOL.** See OILS, VOLATILE.

**CASHEIN.** See PROTEIDS.

**CASSIA OIL.** See OILS, VOLATILE.

**CASTOR OIL.** This oil rotates a ray of polarised light. 10 p. c. solutions of pure Italian and Ostend castor oil in absolute alcohol gave, as a mean result, a direct deviation of  $10^\circ$  to the right, which gives as the specific rotatory power of castor oil,  $(\alpha) = +12.15^\circ$ . This behaviour of castor oil may be used as a test of its purity, although the specific rotatory power is too small to allow small quantities of adulteration to be detected. Castor oil also contains a constant quantity of nitrogen, which may be due to the presence of an alkaloid. It is possible indeed, that not only the purgative properties, but also the circular polarisation, are due, not to the oil itself, but to the presence of this alkaloid (Popp. *Arch. Pharm.* [2] cxlv. 233).

**CATHARTIN.** This substance, extracted from senna by Lassaigne & Berthelot (1st Suppl. 817), and by them regarded as the active principle of the plant has

lately been examined by Bourgoïn (*Compt. rend.* lxxiii. 1449), who finds that it is a mixture of three distinct substances, viz.:—

1. *Chrysophanic Acid*.—Obtained by exhausting crude cathartin with ether; it is present but in small quantity in senna, but may be at once rendered evident by the formation of a characteristic red colour on the addition of ammonia to an aqueous infusion of the leaves.

2. *A dextro-rotatory Glucose*.—Cathartin freed from the above acid yields with water a limpid solution, possessing the following properties: (1.) It ferments in contact with yeast, giving carbonic anhydride and alcohol. (2.) It reduces a cupropotassic solution. (3.) Freed from chrysophanine and colouring matter, it rotates a ray of polarised light to the right. This glucose may be isolated by precipitating with basic lead acetate, and evaporating to dryness after removing the dissolved lead.

3. *Chrysophanine*.—Obtained by adding lead acetate to a strong infusion of senna, after the removal of the mucilaginous matter by alcohol, decomposing the precipitate with hydrogen sulphide, evaporating the liquid to a syrup, treating the syrup with alcohol, dissolving the residue in water, reprecipitating with alcohol, and then drying over sulphuric acid. Thus obtained it is almost white.

**CELLULOSE.** The solubility of this substance in ammoniacal copper-solution has been made available for the preparation of water-proof paper, artificial wooden slabs, &c.

When linen rags or wood sawdust are fully dissolved in ammoniacal copper-solution, and the solution then allowed to evaporate to dryness, a semi-transparent, brittle glass is left. But if the action of the solvent be prevented from effecting more than a commencing superficial solution, in which the fibres maintain their original form and disposition, a very tough material is obtained. A sheet of paper, left only an instant in the ammoniacal copper-solution, and then passed between rollers and dried, becomes quite impervious to water, and does not lose its power of cohesion at the boiling heat. Two sheets of paper thus treated adhere firmly together, and form one piece, and by treating a large number of sheets of paper in the same manner, artificial boards are produced. Linen pieces thus treated furnish a very elastic material of great cohesive power. By treating linen and paper together in this manner, a material is obtained of great firmness and strength, which is said to be well adapted for making roofing tiles, gas and water pipes, articles of clothing, and even for boats (*Dingl. polyt. J.* ccliv. 514).

*Animal Cellulose*.—Schäfer (*Ann. Ch. Pharm.* clx. 312), from his analyses of the mantles of the *Pyrosomida*, *Salpida*, and *Phallusia mamillaris*, finds that the cellulose, or tunica (v. 918) derived from them is identical with vegetable cellulose. The mantles, after being boiled in a Papin's digester to remove chondrigen, were treated with dilute hydrochloric acid to remove the inorganic constituents. These consisted of calcium sulphate, sodium sulphate, and traces of iron, calcium carbonate, and calcium phosphate. The mantles were then boiled for several days in a saturated solution of caustic potash, and subsequently washed with alcohol and water. The mantles so treated retained their original form, but had become transparent like glass, but not horny, as Berthelot found in *Cynthia papillata*. The substance thus obtained is quite free from nitrogen, and contains 44.09 p. c. carbon, 6.30 hydrogen, and 49.61 oxygen.

With iodine and sulphuric acid it gives a violet colour like vegetable cellulose. It is soluble in ammonio-cupric oxide, from which it is precipitated like cellulose by acids. The precipitate is soluble in dilute hydrochloric acid, and gives the cellulose reaction with iodine and zinc chloride. It is converted into sugar by prolonged heating with dilute sulphuric acid in closed tubes. Like vegetable cellulose, it is converted into pyroxylin by the action of fuming nitric acid. The mantles so converted into pyroxylin retain their form, but are very brittle. They are soluble in ether, which on evaporation leaves a film like the ordinary collodion film. These reactions leave little doubt of the complete identity of animal and vegetable cellulose.

**CEMENTS.** A good cement for broken glass and porcelain basins may be prepared by soaking half an ounce of isinglass in distilled water, then pouring off the water, and adding so much alcohol as just to cover the isinglass, the solution being promoted by heat. A quarter of an ounce of mastic is then dissolved in three quarters of an ounce of alcohol; the two solutions are mixed; a quarter of an ounce of powdered gum-ammoniac is added; and the mixture, after being well shaken, is evaporated in a water-bath to the consistence of strong glue. The cement thus prepared is poured into a glass in which it soon solidifies to a jelly, and is then ready for use. It is warmed just before using, and is applied with a brush to the perfectly clean, warm, fractured surface; it hardens in 24 hours (*Dingl. polyt. J.* ccliv. 344).

*Hydraulic Lines and Cements*.—Roman and Portland Cements are compounds of

alumina, lime, and silica in closer or looser combination according to the temperature at which they have been burnt. Besides the constituents above named, magnesia, potash, soda, and generally sulphuric and phosphoric acids are also present. Of these subsidiary bodies, sulphuric acid (as gypsum) is so hurtful to the quality of the cement, that if a sample contains any considerable quantity—even 3 p. c.—it should be rejected. The gypsum is burnt dead at the temperature employed in making the cement, and does not combine with water until after the rest of the mass has hardened, and then, as it slowly takes up water and expands, it causes the whole to crumble. Much magnesia seems also to injure the quality, but a moderate proportion of soda improves it (C. Bender, *Dingl. polyt. J.* cii. 254).

Wartha (*ibid.* ciii. 527) found that the hardening power of a natural hydraulic lime, made from a somewhat siliceous marl, was not impaired by mixing it with even 15 p. c. of nearly pure unslaked lime, but that when ferruginous siliceous lime was added, the mass, after binding, fell to powder when immersed in water. This effect appears to be due to the circumstance that the slaking of the impure dead-burnt lime does not take place till after the cement has set, and that the consequent swelling causes the mass to break up.

According to Knapp (*ibid.* ciii. 513) the hydraulic properties of a cement depend as much on its mechanical state as on its chemical composition. Schott has shown that the coarse, sandy parts of Portland cement have but slight power of hardening under water, but if they be rubbed to a fine powder, this powder exhibits all the properties of the original fine cement.

*The so-called Scott's Cement.*—It was observed some years ago by Captain H. Scott that quicklime heated to redness in the vapour of burning sulphur lost its power of slaking, but acquired the property of gradually hardening when stirred up in water. F. Schott (*Dingl. polyt. J.* ciii. 52) has examined the mode of formation of the cement thus produced, with the view of determining the nature of the compound formed, and the best mode of preparing it. His principal results are: that cold dry lime does not absorb cold dry sulphur dioxide, but that at a red heat complete absorption takes place without evolution of gas; that when sulphur dioxide is passed over red-hot lime contained in a tube, combination takes place, attended with evolution of light and heat, the product being a mixture of sulphate and sulphide of calcium, with excess of lime in uncertain proportion; that when calcium sulphite is heated to moderate redness, it is resolved into sulphate and sulphide, according to the equation  $4\text{CaSO}_3 = 3\text{CaSO}_4 + \text{CaS}$ , forming a mass devoid of hydraulic properties, but that when heated to whiteness it sinters, leaving a mass containing only about half the sulphur required by the above formula, and capable of hardening under water.

A mass having all the properties of Scott's cement may be prepared by strongly igniting a mixture of gypsum and lime, in the proportion of 2 mols. of the former to 3 mols. of the latter. The cement so formed is the better the higher the temperature at which it has been formed, and the less calcium sulphite it contains.

*Cement-stone found near Jena.*—This stone, which is largely used for the manufacture of cements, contains about 90 p. c. of matter, chiefly earthy carbonates, soluble in hydrochloric acid. The composition of the soluble portion is as follows:

$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{CaSO}_4$	$\text{FeO}$	$\text{FeO}$	$\text{MnO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{SiO}_2$	$\text{H}_2\text{O}$
49.84	26.96	0.36	3.83	4.17	0.22	0.40	0.35	2.96	0.66 = 89.75.

These numbers show that the dolomitic constituents of the stone may be nearly represented by the formula  $2\text{MgCO}_3 \cdot 3\text{CaCO}_3$ .

The residue, insoluble in hydrochloric acid, after being freed from soluble silica by digestion in sodium carbonate was found to contain:—

Potassium Silicate	Sodium Silicate	Calcium Silicate	Magnesium Silicate	Ferric Silicate	Aluminium Silicate	Sand
0.26	0.47	2.01	0.16	0.95	3.04	3.26 = 10.45

The oxygen ratio in the metallic oxides and the silica, viz.,  $\text{RO} : \text{R}'\text{O}_2 : \text{SiO}_2 = 1 : 2.7 : 3.8$  leads to the formula  $\text{RO} \cdot \text{SiO}_2 + \text{R}'\text{O}_2 \cdot \text{SiO}_2$ , which is that of zeolite, natrolite and labradorite (E. Reichardt, *Dingl. polyt. J.* cc. 219).

**CERITE METALS.** The atomic weights of these metals have lately been discussed by Mendeleeff in his paper 'Ueber die periodische Gesetzmässigkeit der chemischen Elemente,' (*Ann. Ch. Pharm. Suppl.* viii. 186). For the atomic weights hitherto received, viz.  $\text{C} = 92$ ,  $\text{La} = 92$ ,  $\text{Di} = 95$ , he proposes to substitute  $\text{Ce} = 138$ ,  $\text{La} = 180$ ,  $\text{Di} = 138$ . His reasons for proposing this change are founded chiefly on the differences between the observed properties of these metals and those which, if their received atomic weight were correct—they might be expected to have according to Mendeleeff's system of classification of the elements (see ELEMENTS).



With regard to cerium in particular, Mendeleeff points out that there are but two known oxides of this metal, not three, as usually stated, the so-called ceric oxide ( $\text{Ce}^{\text{IV}}\text{O}_2$ ) being purely hypothetical, as it has never been obtained in the separate state, and no salts corresponding with it in composition are known. The two known oxides  $\text{CeO}$  and  $\text{CeO}^{\text{II}}$ , according to the atomic weight  $\text{Ce} = 92$ , become  $\text{Ce}^{\text{IV}}\text{O}_2$  and  $\text{Ce}^{\text{III}}\text{O}^{\text{I}}$  or  $\text{CeO}^{\text{II}}$ , if the proposed atomic weight 138 is adopted. Mendeleeff has made a determination of the specific heat of cerium (semifused and dried in hydrogen), which he finds to be 0.050. This number multiplied by 138 gives, for the atomic heat the product 6.9, which is much nearer to the mean value of the atomic heats of the elements, than that obtained with the commonly received atomic weight of cerium, viz.  $0.05 \times 92 = 4.6$ .

On the other hand, Rammelsberg (*Deut. Chem. Ges. Ber.* vi. 81) objects to the proposed change: (1). Because if there are but two oxides of cerium,  $\text{CeO}$  and  $\text{CeO}^{\text{II}}$  (or  $\text{Ce}^{\text{IV}}\text{O}_2$  and  $\text{Ce}^{\text{III}}\text{O}^{\text{I}}$ ) these oxides will exhibit the unusual oxygen-ratio 3 : 4. (2). If the higher oxide is to be regarded as an independent oxide  $\text{CeO}^{\text{II}}$  (or  $\text{CeO}^{\text{IV}}$ ) and not as a compound of monoxide and sesquioxide,  $\text{CeO} \cdot \text{CeO}^{\text{II}}$ , it ought to form analogous salts, e.g.  $\text{Ce}^{\text{III}}(\text{SO}^{\text{IV}})^{\text{I}}$  or  $\text{CeO}^{\text{II}} \cdot 4\text{SO}^{\text{IV}}$ , or  $\text{Ce}^{\text{IV}}\text{SO}^{\text{IV}} \cdot (\text{Ce}^{\text{IV}})^{\text{I}}(\text{SO}^{\text{IV}})^{\text{I}}$ , whereas in nearly all the known ceroso-ceric salts, the proportion of  $\text{Ce}^{\text{IV}}$  and  $(\text{Ce}^{\text{IV}})^{\text{I}}$  is different from this (v. 586); thus the ceroso-ceric sulphate which crystallises in brown-red hexagonal forms, has the composition  $\text{Ce}^{\text{IV}}\text{SO}^{\text{IV}} + 18 \text{ aq.}$ , or  $\frac{3\text{CeSO}^{\text{IV}}}{\text{Ce}^{\text{IV}}(\text{SO}^{\text{IV}})^{\text{I}}_3} + 18 \text{ aq.}$

The reduction of the higher to the lower oxide of cerium is regarded by Mendeleeff as analogous to that of  $\text{TiO}^{\text{IV}}$  to  $\text{Ti}^{\text{III}}\text{O}^{\text{II}}$ ; but ceroso-ceric oxide is reduced to cerous oxide by hydrochloric acid, with evolution of chlorine, which is not the case with titanic oxide. Cerous oxide decomposes solution of sal-ammoniac, an effect not produced by sesquioxides,  $\text{M}^{\text{III}}\text{O}^{\text{II}}$ . Lastly ceroso-ceric oxide crystallises in the regular system, like most oxides of the form  $\text{MO} \cdot \text{M}^{\text{III}}\text{O}^{\text{II}}$ , whereas, according to Mendeleeff's formula  $\text{CeO}^{\text{II}}$ , it should be isomorphous with  $\text{TiO}^{\text{IV}}$  and  $\text{ZrO}^{\text{IV}}$ .

For didymium and lanthanum Mendeleeff proposes the atomic weights  $\text{Di} = 138$ ,  $\text{La} = 180$ , giving to the respective oxides the formulæ  $\text{Di}^{\text{IV}}\text{O}_2$  and  $\text{LaO}^{\text{IV}}$ , whereas both are usually regarded as monoxides. In favour of the dissimilar formulæ of these oxides, Mendeleeff adduces the fact, communicated to him by Marignac, that none of the corresponding salts of didymium and lanthanum are isomorphous; that didymium sulphate separates easily and nearly pure from a mixed solution of the two sulphates; and that the formulæ commonly given to these sulphates are not analogous, that of the didymium salt being  $3\text{DiSO}^{\text{IV}} \cdot 8\text{H}_2\text{O}$ , and that of the lanthanum salt  $\text{LaSO}^{\text{IV}} \cdot 3\text{H}_2\text{O}$ . The unusual formula  $3\text{DiSO}^{\text{IV}} \cdot 8\text{H}_2\text{O}$  will be changed according to Mendeleeff's atomic weight, into  $\text{Di}^{\text{IV}}(\text{SO}^{\text{IV}})^{\text{I}}_3 \cdot 8\text{H}_2\text{O}$ . That the dissimilarly constituted oxides  $\text{CeO}^{\text{IV}}$ ,  $\text{Di}^{\text{IV}}\text{O}_2$ ,  $\text{LaO}^{\text{IV}}$  should constantly occur together in nature, need occasion no surprise, inasmuch as many similar cases are known, e.g. the simultaneous occurrences of  $\text{Nb}^{\text{IV}}\text{O}_2$  and  $\text{TiO}^{\text{IV}}$ , of  $\text{W}^{\text{IV}}\text{O}_3$  and  $\text{Nb}^{\text{IV}}\text{O}_3$ , and of  $\text{V}^{\text{IV}}\text{O}_2$  and  $\text{CrO}^{\text{IV}}$ .

On the other hand, Rammelsberg states, as the result of his own observations, that sulphate of didymium is isomorphous with the sulphates of yttrium and cadmium, the general formula of these sulphates being  $3\text{R}^{\text{IV}}\text{SO}^{\text{IV}} + 8 \text{ aq.}$ ; hence he infers that, according to Mendeleeff's view, cadmium oxide should also be a sesquioxide  $\text{Cd}^{\text{IV}}\text{O}_2$ ; and since greenockite, wurtzite, and cinnabar are also isomorphous, the oxides of zinc and mercury should also be  $\text{Zn}^{\text{IV}}\text{O}_2$  and  $\text{Hg}^{\text{IV}}\text{O}_2$ . Rammelsberg regards the isomorphism of the three cerite metals as positively established, and hence concludes that the oxide of lanthanum must be analogous in composition to cerous oxide and didymium oxide.

According to Mendeleeff's view, however, lanthanum oxide and ceroso-ceric oxide should be isomorphous, since their formulæ are  $\text{LaO}^{\text{IV}}$  and  $\text{CeO}^{\text{IV}}$ , whereas in reality, lanthanum oxide is trimetric, like  $\text{PbO}$  and  $\text{CuO}$ , while ceroso-ceric oxide is monometric. Again, lanthanum oxide dissolves easily in hydrochloric acid, whereas ceroso-ceric oxide dissolves slowly and with reduction. The chlorides of the cerite metals also, which, according to Mendeleeff, are  $\text{Ce}^{\text{IV}}\text{Cl}^{\text{I}}$ ,  $\text{Di}^{\text{IV}}\text{Cl}^{\text{I}}$  and  $\text{LaCl}^{\text{I}}$ , are very much alike, are probably isomorphous when they crystallise with 4 aq., and are very different in character from the volatile chlorides  $\text{RCl}^{\text{I}}$  and  $\text{ROCl}^{\text{I}}$  which are decomposed by water, such as  $\text{TiCl}^{\text{I}}$  and  $\text{Ti}^{\text{III}}\text{Cl}^{\text{I}}$ .

For all these reasons Rammelsberg is of opinion that the changes proposed by Mendeleeff in the atomic weights of the cerite metals cannot be admitted.

**CERIUM.** The following method of preparing pure cerium salts is given by C. Erk (*Zeitschr. f. Chem.* [2] vii. 100):—Finely powdered cerite is made into a thin paste with sulphuric acid, kept warm for several hours, and then gently heated; the white powder is then exhausted by repeated treatment with boiling dilute nitric acid; the filtered solution, after treatment with sulphydric acid, and filtration, is mixed with a little hydrochloric acid and oxalic acid; the oxalates are ignited in a platinum dish.

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with constant stirring, and dissolved in rather strong nitric acid; the solution is evaporated to a syrupy consistence, and then mixed with a large quantity of boiling dilute sulphuric acid; and the precipitate of basic ceroso-ceric sulphate is washed with hot water as long as the washings give a precipitate with oxalic acid.

The addition of magnesia to the oxalates previous to ignition, as recommended by Bunsen and by Jögel, is unnecessary; it is also very difficult to separate the magnesia perfectly from the ignited product.

Popp's method (1st Suppl. 419), which consists in treating a solution containing cerium, lanthanum, and didymium with chlorine and sodium acetate, is efficient for the preparation of pure cerium salts, but not for the preparation of pure lanthanum and didymium compounds, on account of the easy reducibility of ceroso-ceric oxide by free acetic acid. The precipitate described by Popp as a peroxide of cerium, is according to Erk, a basic acetate.

**Electrolysis of Cerium Salts.**—A concentrated solution of cerous chloride subjected to the action of a Bunsen's battery of three elements gave free chlorine at the positive, and a deposit of ceroso-ceric hydrate at the negative pole. Fused cerous chloride gave, at the negative pole, small quantities of metallic cerium, together with reddish white laminae of cerium oxychloride (formed by the action of atmospheric moisture). At the positive pole (consisting of gas carbon) hydrogen chloride was evolved, a larger quantity of ceroso-ceric oxide was formed, and the resulting mass, when treated with water, gave off a very fetid gas. Strong solutions of cerous sulphate turned yellow at the positive pole, from formation of ceroso-ceric sulphate, while at the negative pole there was formed, besides a little metallic cerium, a waxy deposit of ceroso-ceric sulphate which afterwards became crystalline. The electrolysis of a neutral solution of cerous nitrate yielded, at the negative pole, a brownish yellow mass, and a quantity of ammonia sufficient to precipitate the whole of the cerium. An aqueous solution of cerous acetate yielded a basic acetate which dried up to brownish amorphous lumps. Neither of these reactions yielded an oxide of cerium higher than ceroso-ceric oxide  $\text{Ce}^{\text{IV}}\text{O}^{\text{II}}$  (Erk, *loc. cit.*).

**Cerous Platinochloride.**—A salt having the composition  $2\text{CeCl}_2 \cdot 3\text{PtCl}_4 + 8\text{H}_2\text{O}$  is described by Holzmänn (i. 333). Another containing  $4\text{CeCl}_2 \cdot 3\text{PtCl}_4 + 36\text{H}_2\text{O}$  has lately been obtained by Marignac (*Ann. Ch. Phys.* [4] xxx. 65), from a solution containing excess of platine chloride. It is very soluble in water, and crystallises only from syrupy solutions, redissolving on the slightest rise of temperature. It forms dimetric crystals,  $\text{P.O.P}$ , having the angle  $\text{P} : \text{P}$  in the lateral edges =  $121^\circ 40'$  to  $122^\circ$  and  $\text{oP} : \text{P} = 106^\circ$  to  $106^\circ 20'$ . The crystals are orange-red, deliquesce in moist air, but effloresce in the air of a warm room during cold dry days. They give off half their water at  $100^\circ$ .

Marignac has also obtained platinochlorides of lanthanum and didymium, isomorphous with the cerium salt.

**Oxides.** When pulverised cerite is heated with strong sulphuric acid and then treated with water, an abundant evolution of hydrogen takes place; and this effect is renewed if the cerite, after the lapse of a considerable time (about a year), be again treated with the acid and water. This effect appears to be due to a power possessed by the lower oxides present in the mineral of decomposing water in presence of strong acids, whereby they are raised to a higher state of oxidation (Sonnenschein, *Deut. Chem. Ges. Ber.* iii. 632).

**Ceroso-ceric oxide** is a more powerful oxidising agent than most oxides represented by the formula  $\text{M}^{\text{IV}}\text{O}^{\text{II}}$ , and this power is attributed by Sonnenschein to the peculiar state of the oxygen contained in it. He observes that when ceroso-ceric oxide is treated with strong sulphuric acid, the odour of ozone is evolved, and the presence of ozone may be further rendered evident by its well-known reactions. The oxide forms with sulphuric acid, a brown-red solution which may be used in place of permanganate for the titration of iron, inasmuch as it is very permanent, and indicates the termination of the oxidation by a distinct change of the brown-red colour of the solution to a light salmon-colour. The same solution may be used for decomposing the excess of sulphuretted hydrogen produced in many operations of chemical analysis.

Ceroso-ceric oxide added to *strychnine* previously mixed with strong sulphuric acid, produces a fine blue colour which affords a very delicate test for the presence of *strychnine*. It does not produce the same colour with any other alkalioid, (see *ANALYSES*, p. 43).

**Nitrates.** A solution of ceroso-ceric hydrate in nitric acid mixed with nitrate of magnesium or zinc, yields red rhombohedral crystals of a double salt, having, according to Holzmänn's analysis (*J. pr. Chem.* Lxxv. 330), the composition  $2\text{Ce}^{\text{IV}}\text{O}^{\text{II}} \cdot \text{Ce}^{\text{IV}}\text{N}^{\text{O}}_3 \cdot (\text{Ce}^{\text{IV}}\text{N}^{\text{O}}_3)_2 + 15 \text{ aq.}$  Zschiesche, however, (*ibid.* cvii. 54) found that the

green nickel salt prepared in like manner, and crystallising in the same form, is not a ceroso-ceric but a cerous salt  $\text{Ni}^{\text{N}^{\circ}\text{O}^{\circ}}\text{Ce}^{\text{N}^{\circ}\text{O}^{\circ}} + 8 \text{ aq.}$ , and that analogous double salts containing cobalt and manganese may be prepared in a similar manner. He attributes Holzmänn's result to a defect in the method of analysis, which consisted in precipitating the cerium oxide directly from the solutions, washing it, and, then determining the quantity of ceric oxide present by treatment with hydrochloric acid. Now a precipitate of cerous oxide thus formed oxidises very quickly in contact with the air; but the oxidation may be completely prevented by mixing the solution before precipitation, with a large excess of sal-ammoniac, and treating the precipitate with hydrochloric acid without first drying it. Operating in this manner Zschiesche found that the double nitrates above mentioned contained only cerous, no ceric oxide. Rammelsberg has also analysed the ceroso-magnesium nitrate and finds its formula to be exactly analogous to that of the nickel salt, viz.  $\text{MgN}^{\circ}\text{O}^{\circ}\text{Ce}^{\text{N}^{\circ}\text{O}^{\circ}} + 8 \text{ aq.}$  He finds that the red magnesium salt analysed by Holzmänn, and designated by Bunsen as magnesio-ceric nitrate, becomes pale yellow after one recrystallisation, and nearly colourless after two, and therefore considers that this salt owes its red colour merely to the ceric mother-liquor with which the crystals are drenched.

**Basic Ceroso-ceric Acetate.** The light yellow precipitate obtained in Popp's method of separating cerium from the allied metals is, according to Erk (*Zeitschr. f. Chem.* [2] vii. 115), a basic acetate having the composition  $\text{C}^{\text{H}}\text{Ce}^{\text{O}}\text{O}^{\text{O}}$ . It is easily soluble in water, but insoluble in dilute aqueous sodium acetate.

**Cerous Oxalate** dried at ordinary temperatures has the composition  $\text{CeC}^{\text{O}}\text{O}^{\circ} + 4\text{H}^{\circ}\text{O}$ ; after drying at  $100^{\circ}$  it contains  $\text{CeC}^{\text{O}}\text{O}^{\circ} + \text{H}^{\circ}\text{O}$ . The last molecule of water cannot be expelled without decomposing the salt (Erk).

**Sulphates.** Marignac some years ago described a cerous sulphate,  $\text{CeSO}^{\circ}$ .  $8\text{H}^{\circ}\text{O}$ , crystallising in right rhombic octahedrons (*Recherches sur les formes cristallines de quelques composés chimiques*, Genève, 1855). Czudnowicz, on the other hand (*J. pr. Chem.* xxx. 19), obtained a trihydrated cerous sulphate in the form of hexagonal prisms; and this result was corroborated by Hermann (*ibid.* xcii. 126), who, moreover, obtained another cerous sulphate in octahedral crystals having the composition  $3\text{CeSO}^{\circ}\cdot 8\text{H}^{\circ}\text{O}$ , analogous to that of didymium sulphate; the two salts being formed under the same circumstances, namely, by the evaporation of a solution of cerous sulphate at a gentle heat. Recent observations by Marignac (*Ann. Chim. Phys.* [4] xxx. 57) have shown that these statements are correct, and that the octahedral  $\frac{8}{3}$ -hydrated salt is formed most readily by evaporation in a vacuum at ordinary temperatures—the hexagonal trihydrated crystals by evaporation in the air at  $40^{\circ}$ – $50^{\circ}$ .

The crystals of the salt  $3\text{CeSO}^{\circ}\cdot 8\text{H}^{\circ}\text{O}$  have the faces P . 2P, predominant,  $\infty \text{P} \propto$ .  $4\text{P} \propto$ , and others subordinate. The principal angles are as follow:

In the Brachydiagonal principal section	In the Macrodiaagonal principal section	In the Basal principal section
P : P = $114^{\circ}12'$	$111^{\circ}10'$	$103^{\circ}14'$
2P : 2P = $99^{\circ}48'$	$95^{\circ}48'$	$136^{\circ}17'$

Notwithstanding the analogy of composition between this salt and the sulphate of didymium, the two salts are not isomorphous, the crystals of the didymium salt being monoclinic.

The crystals of the hexagonal salt,  $\text{CeSO}^{\circ}\cdot 3\text{H}^{\circ}\text{O}$ , are mostly combinations of the hexagonal prism  $\infty \text{P}$  with the pyramid P, sometimes also with  $\frac{1}{2}\text{P}$ , and two secondary pyramids (see CRYSTALLOGRAPHY, ii. 138). Angle  $\infty \text{P}$  :  $\infty \text{P} = 120^{\circ}$  to  $120^{\circ}15'$ ;  $\infty \text{P}$  : P =  $130^{\circ}10'$ ;  $\infty \text{P}$  :  $\frac{1}{2}\text{P} = 112^{\circ}55'$ . This salt is isomorphous with the corresponding sulphate of lanthanum.

**Ceroso-ceric Sulphates.**—The red hexagonal crystals which separate by slow evaporation from a solution of ceroso-ceric oxide in sulphuric acid, consist, according to Rammelsberg (v. 587), of  $3\text{CeSO}^{\circ}\text{Ce}^{\text{O}}(\text{SO}^{\circ})^{\circ} + 18 \text{ aq.}$  Zschiesche, on the other hand, (*J. pr. Chem.* cvii. 65; *Zeitschr. f. Chem.* [2] vii. 40) assigns to them the composition,  $6\text{CeO}\cdot 6\text{SO}^{\circ} + \text{Ce}^{\text{O}}\text{O}^{\circ}\cdot 3\text{SO}^{\circ} + 27 \text{ aq.}$ , or perhaps  $5(\text{CeO}\cdot \text{SO}^{\circ}) + 2(\text{CeO}^{\circ}\cdot 2\text{SO}^{\circ}) + 27 \text{ aq.}$  Rammelsberg (*Dout. Chem. Ges. Ber.* vi. 85.), from a fresh analysis of the salt in well-defined crystals, deduces the formula  $3\text{CeSO}^{\circ}\text{Ce}^{\text{O}}(\text{SO}^{\circ})^{\circ} + 21 \text{ aq.}$ , which, agrees with his earlier formula, excepting in the amount of water.

From the mother-liquors of the hexagonal salt, or from a solution of ceroso-ceric hydrate in dilute sulphuric acid, there is deposited a yellow salt, not in measurable crystals, which, according to Rammelsberg, has the composition  $\text{Ce}^{\text{O}}\text{S}^{\circ}\text{O}^{\circ} + 8 \text{ aq.}$  or  $\text{CeSO}^{\circ}\text{Ce}^{\text{O}}(\text{SO}^{\circ})^{\circ} + 8 \text{ aq.}$ ; according to Erk it contains 14 aq.

The yellow basic salt formed from either of the preceding by the action of water, appears to lose acid by long keeping; hence the formula assigned to it (v. 587) viz.  $2\text{Ce}^{\text{O}}\text{O}^{\circ}\cdot 3\text{SO}^{\circ} + 8 \text{ aq.}$  must be regarded as uncertain. According to Erk, this salt is

decomposed by washing with hot water, and loses all its sulphuric acid by repeated boiling with water. When washed with cold water, pressed between filter-paper, and dried over oil of vitriol, it has the composition  $\text{Ce}^2\text{HSO}_4 + 2\text{aq.}$  or  $2\text{CeSO}_4 \cdot \text{Ce}^2\text{O}^3 \cdot 11\text{H}_2\text{O} + 4\text{aq.}$

*Compounds of the Cerium Sulphates with Luteo-cobaltic and Rosco-cobaltic Sulphate.* When a hot, strongly acid solution of ceroso-cerie sulphate\* is mixed with a hot saturated acid solution of luteo-cobaltic sulphate, a light yellow crystalline precipitate is formed, which the microscope shows to be made up of hexagonal prisms. After washing with a small quantity of cold water, it has the composition  $12\text{NH}_4 \cdot \text{Co}^2(\text{SO}_4)^2 \cdot \text{Ce}^2(\text{SO}_4)^2 \cdot 11\text{H}_2\text{O}$ . It may be heated to  $150^\circ$  without decomposition.

The corresponding *cerous salt*  $12\text{NH}_4 \cdot \text{Co}^2(\text{SO}_4)^2 \cdot 3\text{CeSO}_4 \cdot 11\text{H}_2\text{O}$  is obtained by adding a hot concentrated solution of luteo-cobaltic sulphate to a hot nearly neutral solution of cerous sulphate as long as the supernatant liquid remains colourless. A yellow precipitate is then formed, having a somewhat paler colour than the ceric salt just described, but resembling it in form, so that the two salts appear to be isomorphous.

*Rosco-cobaltic double salts* of analogous composition have likewise been obtained, but they are very easily decomposed by water. The compound  $10\text{NH}_4 \cdot \text{Co}^2(\text{SO}_4)^2 \cdot \text{Ce}^2(\text{SO}_4)^2 \cdot 5\text{H}_2\text{O}$  is produced as an orange-brown crystalline precipitate, by adding a solution of ceroso-cerie sulphate to an excess of a hot, strongly acid solution of rosco-cobaltic sulphate, or by adding the latter to an excess of the cerium salt. The crystals belong to the regular system. The corresponding *cerous salt* is obtained as a homogeneous precipitate, only when a solution of cerous sulphate is added to a large excess of rosco-cobaltic sulphate. The crystals, which resemble those of the ceric salt, have the composition  $10\text{NH}_4 \cdot \text{Co}^2(\text{SO}_4)^2 \cdot 3\text{CeSO}_4 \cdot 5\text{H}_2\text{O}$ . An attempt to prepare a corresponding lanthanum salt was unsuccessful. The amount of cerium in these salts appears to vary within certain limits, and the rosco-cerie salt appears to be always mixed with a certain quantity of cerous salt.

It was not found possible to prepare ceroso-cerie oxide free from didymium by oxidising a solution of cerous salt with lead dioxide and sulphuric acid, and then mixing it with luteo-cobaltic sulphate, the double salt thereby produced always retaining a certain quantity of didymium (C. H. Wing, *Sill. Amer. J.* [2] xl. 356).

**CERULEOLACTIN.** A hydrated aluminium phosphate,  $3\text{Al}^2\text{O}^3 \cdot 2\text{P}^2\text{O}^5 \cdot 10\text{H}_2\text{O}$ . Intely found in botryoidal and reniform masses in the Rindöberg mine at Katzeclenberg in Nassau (see PHOSPHATES).

**CERUSSITE,**  $\text{PbCO}_3$ . This mineral is known to accompany the galena of Kirilbaba in Bukowina.

Crystals of remarkable beauty have recently been met with, measuring 13 mm. long and 7 mm. broad, and of a yellowish or greyish-white colour. Both as individuals and in groups they are but slightly attached to the quartz or decomposed mica-slate, and consequently exhibit almost perfect development. A prismatic development along the principal axis, and occasionally simultaneously along the brachydiagonal, is generally observed in them. In addition to the three pinacoids, of which the basal is but slightly developed, there are found the often greatly developed prism  $\infty\text{P}$ , in a less degree the brachyprism,  $\infty\text{P}_3$ , the brachydomes  $\frac{1}{2}\text{P}_\infty$ ,  $\text{P}_\infty$ ,  $2\text{P}_\infty$ ,  $3\text{P}_\infty$ ,  $4\text{P}_\infty$ , the pyramid  $\text{P}$ , and, what is new for cerussite, the brachypyramid  $\text{P}_4$ . The orientation of these forms, often apparently very distorted through dissimilar development of faces, is facilitated by an almost constant surface character of individual forms. The macropinacoid always presents a fine vertical striation, sometimes by oscillatory combination with  $\infty\text{P}$ . The brachypinacoid,  $\infty\text{P}_\infty$  has strongly marked horizontal striation, or decreases gradually by the occasional introduction of the faces of the brachydomes; of the latter,  $\text{P}_\infty$  has strong vertical striation. The ratio of the macrodiagonal, brachydiagonal and principal axis is 1.6306 : 1 : 1.1852. The Kirilbaba crystals often bear considerable resemblance to hexagonal combinations, and some resemble the arragonite of Bilin (v. Zepharovich, *Jahrbuch f. Mineralogie*, 1871, 286).

**CERYLIC ETHERS** (Hesse, *Dent. Chem. Ges. Ber.* iii. 637). The white mealy coating which forms on the capsules of the opium poppy (*Papaver somniferum*) after the petals have fallen off, and increases in quantity as the fruit ripens, consists of a waxy substance called *Opium-wax* or *crosin* [? identical with the cerosin of the sugar-cane, i. 836]. In consequence of the method adopted for obtaining opium from the poppy-heads, part of this wax becomes mixed with the drug, and is found in the residue or marc which remains when the opium is exhausted with water. When this marc, after being treated with a little potash-solution to remove resinous colouring matters, is boiled with alcohol, the alcoholic liquor deposits on cooling a considerable quantity of nearly white crystals, which may be freed from adhering base

pounds by dilute hydrochloric acid, and from a peculiar sticky substance by recrystallisation from boiling alcohol.

The wax thus obtained is nearly white, but is still a mixture which cannot be resolved into its constituents by alcohol. The best reagent for the purpose is chloroform, which at the boiling heat dissolves the true wax, and leaves a substance which crystallises in colourless prisms, melts at a temperature above  $200^{\circ}$ , and is probably related to lactacerein and hyoscerin.

On exposing the chloroform solution to a temperature of  $+10^{\circ}$ , it deposits colourless scales; and if the mother-liquor be then cooled down to  $-10^{\circ}$ , another body is obtained crystallising in small prisms. The compound crystallising at  $+10^{\circ}$  may be purified by recrystallisation from chloroform. It then forms white satiny scales composed of flattened prisms, melts at  $82.5^{\circ}$ , resolidifies at  $80^{\circ}$ , and gives by analysis 82.13 p. c. carbon, and 13.73 hydrogen, agreeing with the formula of ceryllic cerotate  $(C^{18}H^{34}O)_2 = C^{37}H^{72}.C^{37}H^{72}O_2$  (i. 837). This ether dissolves easily in boiling alcohol, and separates almost completely in small prisms on cooling. Ether and acetone dissolve a considerable quantity at boiling heat, and deposit the greater part of it on cooling. It is not acted upon by dilute solution of potassium permanganate or by cold strong sulphuric acid, which however blackens it when heated. It is not acted upon by potash-solution, but by fusion with potassium hydrate it is decomposed, yielding a waxy acid; heated on platinum foil, it first melts and then volatilises, giving off a waxy odour and a smoke which is not easily inflamed, but when once set on fire, burns with a bright and very smoky flame.

The second compound, which separates at  $-10^{\circ}$  from the mother-liquor of the preceding, may be sufficiently purified by treating the crystalline mass with a quantity of chloroform not sufficient to dissolve it all, and removing the undissolved portion, which is contaminated with ceryllic cerotate. The chloroform solution thus obtained deposits small dull translucent nodules, which, when recrystallised from boiling alcohol, yield a white powder composed of small prisms melting at  $79^{\circ}$ , solidifying in the crystalline form at  $76^{\circ}$ , and having the composition of ceryllic palmitate  $(C^{18}H^{34}O)_2 = C^{37}H^{72}.C^{16}H^{32}O_2$ . It dissolves in chloroform, alcohol, ether, and acetone somewhat more readily than the preceding, is not attacked by potash-solution, but is easily decomposed by melting potash, yielding a neutral body which melts at about  $100^{\circ}$ , probably ceryllic alcohol, and a crystallisable fatty acid.

**CETYL ALCOHOL,  $C^{18}H^{38}O$ .** This alcohol is known to be easily converted into sebic acid by the action of nitric acid. On the other hand, when a mixture of sebic acid and caustic baryta is submitted to dry distillation, there is formed, besides a hydrocarbon  $C^{18}H^{36}$  boiling at  $124^{\circ}$ , and other products, a solid body, which, by repeated crystallisation from alcohol, may be obtained in white crystals having the properties and composition of cetyl alcohol; it melts at  $40^{\circ}$  and resolidifies at the same temperature (Scherlenner, *Deut. Chem. Ges. Ber.* iii. 616).

**CHALCEDONY.** Some remarkable concretions of chalcedony from Brazil are described by H. Rosenbusch (*Jahrbuch f. Mineralogie*, 1871, 175). They are found in a bed of marl in the valley of the Jahu, a tributary of the Tiété, on the table land of S. Paulo, forming long cylindrical tubes, some 50 mm. long and from 5 to 8 mm. in diameter. They are for the most part well rounded and hollow; the interior is coated with red ochre which contains much organic matter, a tube when heated emitting a strong empyreumatic odour. Some of the flattened tubes are clearly formed by the union of several smaller ones. In a microscopic section of a tube perpendicular to its axis, a fibrous structure is observed, the fibres being uniformly radii; that cut parallel to the axis is finely granular. The tube is coated on the outside with a crust of quartz crystals, which in their turn, are covered with chalcedony, and on which finally, and lying in contact with the marl, is another layer of quartz. These crystals exhibit the one rhombohedron only, the other being altogether absent or but slightly apparent. Other quartz concretions from this region are much contorted, many having dendritic forms. These remarkable structures, which strikingly resemble the industrial limestone of Auvergne, are in all probability of organic origin.

**CHAMOMILE OIL, BLUE.** This volatile oil, obtained from the flowers of the wild chamomile (*Matricaria Chamomilla*) by distillation with water (iii. 858; *Gmelin's Handbook*, xiv. 365) has lately been examined by Kachler (*Deut. Chem. Ges. Ber.* iv. 36).

The crude oil is a mixture. On rectifying it, after distillation in a current of steam, it began to boil at  $105^{\circ}$ , and between this and  $188^{\circ}$  a small quantity of a faintly blue oil, smelling strongly of chamomile, passed over; between  $188^{\circ}$  and  $255^{\circ}$  a second fraction of a somewhat darker colour was obtained. The magnificent blue vapour which characterises this oil was first formed above  $255^{\circ}$ , the temperature rising slowly

to 295°, and 87 grams distilling over. The portion distilling above 295° was still blue, but more syrupy. The temperature then rose above that at which a mercury thermometer could be employed, the vapour became violet, and a thickish, but still blue oil, was obtained. Finally, there remained in the retort 41 grams of a brown tar.

All these fractions, which had an acid reaction, were washed with potash-solution; the wash-water was acidified with sulphuric acid and exhausted with ether; and the strong, unpleasant-smelling residue remaining after distilling off the ether, was dissolved in water, saturated with ammonia, and converted into a silver salt, the analysis of which indicated that the acid is rutic or capric acid  $C^{10}H^{20}O_2$  (anal. 43.1 p.c. C., 6.5 H., 38.4 Ag.; calc. 44.2 C., 6.8 H., 38.7 Ag.).

The first two fractions, after repeated rectification, yielded a liquid boiling at 150°–168°, which had a composition indicated by the formula,  $C^{10}H^{16}O$  (anal. 79.1 p.c. C., 10.8 H.; calc. 79.0 C., 10.5 H.)

The analysis of the portions of higher boiling point (165°–185°) indicated increasing amounts of carbon and hydrogen, the mean of several determinations being 82.93 p.c. C., and 11.10 p.c. H.; probably due to the presence of a hydrocarbon  $C^{10}H^{16}$ , isomeric with oil of turpentine. Bizio's analyses (*Wien. Acad. Ber.* xliii. [2] 292) also lead to the same conclusion.

The blue fraction, after washing and drying over calcium chloride, was repeatedly rectified, and the various portions analysed. The portions of lower boiling point are, as is plainly shown by their colours, the least pure. That obtained between 270°–300° has the purest colour, a magnificent azure-blue, similar to that of an ammoniacal copper-solution. From numerous analyses of this, and from the results obtained by Bizio and Borntrüger (*Ann. Ch. Pharm.* xlix. 243), it is evident that this body is an isomeric or polymeric of camphor.

$C^{10}H^{16}O$		Bornträger.				Bizio.	Kachler.					
						300°	275°	281°	(287°–288°)			289°
C	79.0	79.85	79.81	79.86	78.41	79.8	79.0	78.92	78.5	78.4	79.5	
H	10.6	10.60	10.69	10.89	10.69	10.4	10.3	10.37	10.7	10.7	10.5	

Accurate determinations of the vapour-density could not be obtained, as the oil is partly decomposed when heated for some time above 310°–320°; nevertheless, the experiments prove that the molecular formula is certainly double, and probably twice the empirical camphor formula,  $C^{10}H^{16}O$ .

A comparison of this portion of the chamomile oil, which appears to be pure, with those of the corresponding fraction of the oil obtained by distillation of galbanum by Mössner (ii. 758), shows them to be very similar in properties, though they appear to differ considerably in composition:

Blue Chamomile Oil, 281°–289°.		Blue Galbanum Oil, 289°–290° (Mössner).	
C = 79.25 per cent.		83.74 per cent.	
H = 10.40 per cent.		11.43 per cent.	

Kachler, finds, however, that the galbanum oil is a very variable mixture according to the temperature at which the resin is distilled. It contains varying quantities of a colourless hydrocarbon, which has the composition of turpentine oil, and may be driven off by heating for two or three days at 230°–250°. This hydrocarbon, when purified by distillation, is not identical with the colourless, limpid, turpentine-like galbanum oil obtained by distillation of galbanum in a current of steam. It is less limpid, has a perfectly different, unpleasant odour, and boils at 240°–260°, whereas the latter boils at 160°–165°. The high percentage of carbon in Mössner's blue oil is probably due to an admixture of this hydrocarbon. Kachler found that the blue galbanum oil, after purification from this body &c., gave 79.07 and 80.8 p.c. C., and 10.42 and 10.4 H.; numbers agreeing well with the camphor formula.

On treating chamomile oil with potassium and with phosphoric anhydride in the same way as Mössner treated galbanum oil, the behaviour of the two oils was found to be identical, and the products obtained were of the same composition.

Products of the treatment with potassium:—

From Galbanum oil.				From Chamomile oil.	
$n^{20}C^{10}H^{16}$		Mössner (255°).		Kachler (255°).	Kachler (250°–255°).
C	88.0	88.7	88.8	88.0	88.1
H	11.4	11.3	11.1	11.4	11.8

The vapour-density, determined by Dumas' method, was 14.8, that calculated for  $3C^{10}H^{16}$  being 14.1.

Products of the action of phosphoric anhydride:—

		From Galbanum oil.	From Chamomile oil.
C	$\text{PCl}_5 \cdot \text{H}^+ \text{O}$	Kachler 89.2	Kachler 88.8
H		10.4	10.8

Bearing in mind the extreme difficulty of preparing such bodies in the pure state, the analytical results obtained with the two oils could not perhaps be regarded as perfectly conclusive in favour of their identity, were it not for some characteristic reactions which seem to remove all doubt. On adding an ethereal bromine solution to a dilute ethereal solution of the product from the treatment of the blue chamomile oil with potassium, the liquid becomes, after a short time, azure blue. This colour is not persistent; on the evaporation of the ether (which should be saturated with water,) it turns green, and finally brown. The product from galbanum oil, and the products of the action of phosphoric anhydride on the two oils, all give exactly the same reaction.

On agitation with nitric acid, sp. gr. 1.25, a similar reaction is observed. The brownish colour at first produced soon passes into a deep violet; afterwards oxidation takes place, and the colour disappears.

**CHEMICAL ACTION.** *Coefficient of Chemical Activity or Elective Attraction.* Mills (*Phil. Mag.* [4] xl. 134; xlv. 343), in studying the action of phosphorus oxychloride upon certain nitrates, has found that the decomposition proceeds with a certain degree of uniformity, the analysis of the residual products showing indeed that, in any series of operations with the same nitrate, the ratio between the weights of chlorine retained and phosphoric oxide produced is sensibly constant. This ratio, multiplied into 4.06 or  $\frac{\text{Cl}}{\text{P}_2\text{O}_5}$  is designated by the symbol  $\alpha$ .

The experiments were thus conducted. A weighed quantity of pure anhydrous nitrate was placed in a suitably arranged reaction-tube, a proportion of phosphorus oxychloride (free from hydrochloric acid and non-fuming) was added, and heat gradually applied until the action reached a maximum, a current of *absolutely* dry air passing slowly through the apparatus during the whole operation. When no more coloured gases were expelled, it was judged that the reaction was completed; the excess of oxychloride was then distilled away, and the residue after weighing was dissolved in water and analysed.

The nitrates of silver, lead, thallium, potassium, sodium, lithium, cesium, and rubidium were submitted to experiment. Barium nitrate was not attacked by phosphorus oxychloride. The accompanying table affords an example of the results:—

	I.	II.	III.
Silver nitrate employed . . . .	2.1746	1.0519	2.7633
Residue obtained . . . .	2.1800	1.0589	2.7345
Temperature . . . .	121°	120°	120°
Composition of the residue, viz.,			
Silver nitrate . . . .	40.77	25.96	57.87
Silver chloride . . . .	49.77	61.91	36.44
Phosphoric oxide . . . .	9.47	12.93	6.60
	100.01	100.80	100.91
Hence the values of $\alpha$ are re- spectively . . . .	5.21	4.74	5.47

The residual nitrate is calculated, not by difference, but from the original nitrate on the basis of the chloride found. In the case of the potassium salt, the amount of nitrate obtained by calculation did not even remotely approximate to the undetermined difference, and a determination of the unattacked nitrate by Harcourt's process (iv. 89) was also unsuccessful.\* The analysis of the lithium residues was attended with

\* In Harcourt's process, if the potassium nitrate be mixed with a small proportion of potassium

several inconveniences, inasmuch as the mass in the tube became vesicular, and finally interrupted the passage of air; from this circumstance, the oxychloride never wholly distilled away, and had, consequently, to be determined by another operation. In the case of thallium nitrate, the dichloride, and not the sparingly soluble thallous chloride, was the result of the reaction.

*Mean values of  $\alpha$ —*

Potassium nitrate 2·001	Sodium nitrate 1·70	Thallium nitrate 4·38	Silver nitrate 5·48
Lead nitrate 5·17	Lithium nitrate 1·61	Cæsium nitrate 2·21	Rubidium nitrate 2·38

The numbers to which  $\alpha$  corresponds are ratios and not absolute quantities; they represent the potential energy or dynamical use which can be made of a nitrate; they are obtained under a law of chemical action, and are in themselves independent of any adventitious circumstances of manipulation. When one nitrate surpasses another in the power of fixing chlorine per unit of phosphoric oxide, that is an index of superior chemical activity, or to name the ultimate cause, attraction; and since this attractive effect can be estimated for several nitrates in a series,  $\alpha$  becomes the coefficient of elective attraction of the nitrates.

If  $\alpha$  be divided by the molecular weights,  $\Sigma$ , of the several nitrates calculated to an uniform weight of oxynitryl ( $\text{NO}^3$ ), the following numbers,  $Q$ , are obtained:—

	$\alpha$ .	$\Sigma$ .	$Q$ .
{ Thallious nitrate . . . .	8·76	265·3	30·29
{ Silver " . . . .	5·48	160·94	31·01
{ Lead " . . . .	5·17	165·56	32·02
{ Rubidium " . . . .	2·38	147·40	61·93
{ Cæsium " . . . .	2·21	195·01	88·24
{ Potassium " . . . .	1·99	101·14	50·82
{ Sodium " . . . .	1·70	85·05	50·03
{ Lithium " . . . .	1·61	60·00	42·86

These numbers show that the elective coefficient is directly proportional to the symbolic (molecular) value, and that, with one exception,  $\alpha$  and  $\Sigma$  increase and diminish in regular order; the quotients  $Q$ , therefore, represent the weights of nitrates which correspond with the unit of elective attraction. If these numbers be considered as an incomplete arithmetical series, of which the most probable value of the first term is 6·258, some interesting results are observable. The mean product of symbolic value into the specific heat is 6·246, and the identity of this number with the foregoing term is unmistakable. If  $s$  = specific heat,  $\Sigma s = n \cdot 6·25$ ,  $n$  being integral. But  $Q = n \cdot 6·25$ ; or since the results of experiment show that  $m > n$ , let  $m = x n$ ; then by combining these two equations, we obtain  $\alpha = \frac{1}{x}$  as the expression of the elective attraction in terms of the specific heat.

Again, comparing any two coefficients ( $\alpha$  and  $\alpha'$ ) we have  $\alpha : \alpha' :: \frac{1}{xs} : \frac{1}{x's'}$ , but in several instances  $x = x'$ , as is obvious from the foregoing table. Then  $\frac{\alpha}{\alpha'} = \frac{s'}{s}$ .

The following instances may be adduced in verification of the latter case:—

$$\begin{aligned} \frac{\alpha (\text{potassium nitrate})}{\alpha (\text{sodium nitrate})} &= 1·17 \text{ by the method of ratios.} \\ &= \frac{·2782}{·2388} = 1·17 \text{ by specific heat.} \\ \frac{\alpha (\text{thallious nitrate})}{\alpha (\text{silver nitrate})} &= 1·50 \text{ by the method of ratios.} \\ &= \frac{·1433}{·0942} = 1·53 \text{ by specific heat.} \end{aligned}$$

phosphate, the whole of the nitrate is not decomposed in the ordinary manner, and the apparent yield requires to be multiplied by the number 1·0689. When the phosphate is absent, a normal number is obtained.



That the intensity of elective attraction is proportional to molecular value is a result quite in accordance with ordinary chemical experience.

When silver nitrate is added to a dilute aqueous solution of potassium iodide bromide, and chloride (these salts having been mixed in any proportion), silver iodide, bromide, and chloride are successively precipitated, that is, in the order of their sym-bolic values. Silver chloride may be wholly converted into bromide by digestion with aqueous potassium bromide; and silver bromide is completely transformable into iodide by aqueous potassium iodide. In the formation of salts, baryta has the preference over strontia, and strontia over lime. In the fractional separation of the volatile members of the fatty series  $C^nH^{2n}O^2$ , by Liebig's process, the law is strictly observed, excepting in the case where  $n = 2$ , which is an intelligible anomaly. Houtz's method of separating the non-volatile members of the same series by means of magnesia exhibits the same order. In a mixture of the hydrocarbons  $C^nH^{2n-2}$ , benzene is the last to be chlorinated or nitrated. Warrington has shown the superiority of ferric over aluminic oxide as an absorber of alkalis in soils. In cases of jaundice, taurocholic acid is destroyed in the system before glycocholic acid.

**Chemical Equilibrium of Carbon, Hydrogen and Oxygen** (Berthelot, *Bull. Soc. Chim.* [2] xiii. 99). Carbon dioxide, through which a series of induction sparks is passed, is quickly decomposed, the decomposition increasing up to a certain point, then diminishing, then again increasing, then diminishing, and so on, without approaching any fixed limit. Neither is any constant proportion observed in the extreme limits between which the decomposition varies. Buif and Hofmann (*Chem. Soc. J.* xii. 293) observed that, when the decomposition of the carbon dioxide had gone on to a certain amount, the resulting mixture of carbon monoxide and oxygen was exploded by the spark, and the dioxide was reproduced. Berthelot did not observe this explosion, but thinks it might take place with weaker sparks than those which he employed. He finds that a mixture of 2 vol. carbon monoxide and 1 vol. oxygen no longer explodes when the admixed carbon dioxide amounts to between 60 and 65 p. c. of the total volume, the limit varying, however, according to the intensity of the sparks. Berthelot also confirms the observation of Dalton that a mixture of carbon monoxide and oxygen no longer explodes when it contains less than  $\frac{1}{4}$ th or more than  $\frac{1}{4}$ ths of its volume of carbon monoxide. The limits depend to a certain extent on the intensity of the spark, and in any given mixture the combustion is sometimes complete, sometimes more or less incomplete. The decomposition of carbon dioxide is completely prevented by the presence of a large quantity of oxygen or carbon monoxide. Mixtures of 16.6 CO<sup>2</sup> with 83.4 CO, or of 13.0 CO<sup>2</sup> with 87.0 CO, were found to contain exactly the same quantities of carbon dioxide after the spark had been passed through them for an hour.

The decomposition of aqueous vapour exhibits the same general features as that of carbon dioxide, not approximating to any fixed limit. The presence of an excess of the water-vapour interferes with the union of hydrogen and oxygen. Under the prolonged influence of the spark, a small quantity of hydrogen or of oxygen in presence of a large excess of the other gas is completely converted into water.

With regard to the equilibrium of hydrogen, oxygen and carbon, Berthelot has already investigated the reaction between hydrogen and carbon monoxide (1st *Suppl.* 30). The products of this reaction are carbon dioxide and acetylene.

In presence of a considerable quantity of water-vapour or carbon dioxide, however, no acetylene is formed, whereby the relations are very much simplified. To prevent condensation of water, the reactions were carried on in tubes which were heated to 100° in a current of steam. Two mixtures were experimented on, consisting of

H = 20.0	CO <sup>2</sup> = 20.0	CO = 40.8 vol.
and H = 20.0	CO <sup>2</sup> = 20.0	CO = 21.6 ..

These mixtures are equivalent in composition to the two explosive mixtures,

H = 20.0	O = 10.0	CO = 60.8
and H = 20.0	O = 10.0	CO = 41.6.

After electric sparks had been passed through these gaseous mixtures for half-an-hour, exactly half the carbon dioxide in each was decomposed, with formation of a volume of water-vapour equal to that of the undecomposed gas. The equilibrium resulting from the influence of a series of electric sparks is therefore the same as that which, in Bunsen's experiments on the combustion of carbon monoxide and hydrogen, (1st *Suppl.* 483), is produced by the sudden explosion of similarly constituted mixtures.

**Division of a body between two Solvents**, Berthelot and Jungfleisch (*Compt. rend.* lxxix. 338) have experimented on this subject, by dissolving a substance in one

of the two liquids, then adding a measured volume of the other solvent, and shaking the whole strongly, the temperature being kept constant by means of a water-bath. The quantity of substance dissolved in the liquid was determined from time to time till the results became constant—a state which was sometimes not attained for an hour or two—and the quantity of the substance dissolved in each of the two solvents was then ascertained.

A body brought in contact with two liquids, in each of which it is soluble, always divides itself between them in a simple ratio, however great may be its solubility in one of them, and the excess of the volume of this same solvent. The quantities dissolved simultaneously by the two liquids stand to one another in a constant ratio, called the coefficient of division. This coefficient is independent of the relative volumes of the two liquids, but varies with their concentration and the temperature, as shown by the following experiments:—

#### INFLUENCE OF TEMPERATURE.

*Weight of Succinic acid  
in 10 c. c. of the—*

	Aqueous Solution	Ethereal Solution	Coefficient of Division
{ At 15° . . . . .	0.376	0.060	6.2
{ „ 0 . . . . .	0.376	0.078	4.9
{ „ 15 . . . . .	0.106	0.019	5.5
{ „ 0 . . . . .	0.098	0.019	5.0

These numbers show that the coefficient of division changes with the temperature, but at a very slow rate. Decrease of temperature increases the action of the ether, that is to say, of the more volatile liquid; but it is not yet proved that this law is general.

#### INFLUENCE OF CONCENTRATION.

The coefficient of division varies with the final concentration of the solvents; it is not, however, proportional to the weight of substance dissolved, but increases at a slower rate.

The numbers *w* in the following tables denote the weight in grams of substance dissolved in 10 c. c. of one or the other solvent after agitation.

#### *Succinic acid, Water, and Ether, at 15°.*

In Water ( <i>w</i> )	In Ether	Coefficient of Division <i>C</i>
0.486	0.073	6.6
0.420	0.067	6.3
0.365	0.061	6.0
0.236	0.041	5.7
0.121	0.022	5.4
0.070	0.013	5.2
0.024	„	5.2

$$C = 5.1 + 3 w.$$

#### *Benzoic acid, Water, and Ether, at 10°.*

*Weight of Benzoic acid  
in 10 c.c. of the—*

Aq. Solution	Ether. Solution	Coefficient of Division
0.00304	0.277 ( <i>w</i> )	1 : 91
0.00258	0.227	1 : 88
0.00150	0.119	1 : 80
0.00110	0.078	1 : 71

In this case the action of the ether greatly exceeds that of the water, contrary to what happens in the case of succinic acid. The results may be represented by the formula:

$$\frac{1}{C} = 63 + 100 w.$$

*Oxalic acid, Water, and Ether, at about 11°.*

Aq. Solution ( <i>w</i> )	Ether. Solution	Coefficient of Division C
0.473	0.052	0.0
0.436	0.046	9.5
0.304	0.031	9.8
0.203	0.0205	9.9

The results may be represented by the formula :

$$C = 10.5 - 3.3 w;$$

in which *w* refers to the aqueous solution ; as also in all the following series :—

*Malic acid, Water, and Ether, at about 18°.*

Weight of Malic acid in 10 c. c. of the Aqueous Solution	Coefficient of Division C
4.1	26
2.2	36
1.0	40
0.35	47

$$C = 49 - 5.6 w.$$

*Tartaric acid, Water, and Ether, at about 20°.*

<i>w</i> = 5.26	2.60	1.00	0.4
<i>C</i> = 91	96	120	130

*Acetic acid, Water, and Ether, at about 18°.*

<i>w</i> = 2.0	1.0	0.3	0.1
<i>C</i> = 1.2	1.4	1.8	2.3

The results obtained with malic, tartaric, and acetic acid show that, in very soluble bodies, the coefficient changes with the concentration more rapidly than in less soluble bodies. The cause of this difference is that concentrated solutions of tartaric or acetic acid dissolve ether in other proportions than dilute solutions, so that the actual solvents are not comparable. Sulphuric and hydrochloric acid are dissolved in considerable quantity by ether, only when they are concentrated; if their aqueous solutions are dilute, the quantities of them taken up by ether can no longer be estimated with accuracy.

*Ammonia, Ether, and Water, at about 17°.*

<i>w</i> = 0.71	0.52	0.27
<i>C</i> = 83	100	135

*Bromine, Water, and Carbon Bisulphide.*

<i>w</i> in 10 c. c. water	<i>w</i> in 10 c. c. CS <sup>2</sup>	C
0.176	10.2	1 : 58
0.030	2.46	1 : 82
0.020	1.55	1 : 78
0.0011	0.09	1 : 80

*Iodine, Water, and Carbon Bisulphide, at about 18°.*

<i>w</i> in 10 c. c. water	<i>w</i> in 10 c. c. CS <sup>2</sup>	C
0.0041	1.74	1 : 420
0.0032	1.29	1 : 400
0.0016	0.66	1 : 410
0.0010	0.41	1 : 410
0.00017	0.076	1 : 440

The coefficient of division of iodine between water and carbon bisulphide may be regarded as independent of the concentration.

*General Laws and Theory of the Preceding Phenomena* (Berthelot, *Ann. Chim. Phys.* [4] xxvi. 408).—The fact that the coefficient of division is independent of the relative volumes of the two solvents when the latter form two distinct layers, is easily explained as follows:—Suppose the dissolved substance to be uniformly distributed in each of the superposed liquids; then, in order that equilibrium may subsist, it is necessary and sufficient that there be equilibrium at the surface of contact of these liquids, as it is there only that the actions take place which cause the dissolved body to pass from one liquid to the other. Consequently the equilibrium cannot be disturbed by addition of a further quantity of either liquid saturated to the same degree by the dissolved body.

The same reasoning is applicable to a multitude of phenomena, in which one and the same body is distributed between different portions of the same system, such as the division of a gas between a liquid and an empty space above; the formation of a saturated vapour in presence of excess of liquid; the solution of a solid body (in excess) in a liquid; and the limited decomposition (dissociation) of a solid or liquid which is giving off gases. All these divisions obey similar laws, because they are determined solely by actions taking place at the surface of separation of two distinct portions of a heterogeneous mass.

2. The coefficient of division appears to approximate to a certain limit as the liquids become more dilute. This coefficient is in fact represented by a formula of the form  $C = M + Nw$ , which approaches nearer and nearer to its first term as  $w$  becomes smaller. This limit may be substituted for the coefficient in all that relates to dilute liquids.

Let  $A$  be the total weight of the body dissolved before any division takes place;  $B$  the weight which remains and the first solvent at the end of the experiment;  $k$  the weight dissolved in the first instance by a given fraction of the second solvent. If now this second solvent be made to act successively in equal fractions, then after  $n$  reactions, the quantity of the soluble substance remaining dissolved in the first liquid will be represented by the relation  $\frac{A}{B} = (1 + k)^n$ , that is to say, it will decrease in

geometric progression. If, on the contrary, the same volume of liquid be used at once, the quantity remaining will be  $\frac{A}{B} = 1 + nk$ . It is therefore advantageous to employ

the second solvent in successive fractions, and the advantage becomes greater as the coefficient  $k$  is larger. The principles which regulate the exhaustion of a dissolved substance by a second solvent are the same as those which apply to the evaporation of a gas dissolved in a liquid (see *Ann. Ch. Phys.* [4] xx. 422).

3. The preceding laws afford the means of determining whether a body dissolved in a liquid is a definite compound or a mixture, namely, by agitating the solution with several successive portions of the second solvent, and determining the coefficient of division at each operation. If the liquid is sufficiently dilute, these successive values of the coefficient will be exactly or nearly equal in the case of a definite compound; but in the case of a mixture of several compounds, these coefficients will vary the more rapidly in proportion as the division-coefficients of the several dissolved compounds differ more from one another, the bodies most soluble in the second solvent, either for example, being eliminated more quickly than the others.

4. The division-coefficient tends towards a certain limit, not only as the liquids become more dilute, but likewise as they become more concentrated, whenever the dissolved body is soluble to a finite extent in each of the liquids. This limit corresponds with the saturation of the two liquids by the dissolved body, and differs more or less from the limit which holds good for the same liquids in the dilute state. At first sight it might appear that this limit of saturated liquids would be expressed by the ratio of the solubilities in the two liquids condensed separately at the same temperature; but it is not so in reality: something, indeed, appears to take place analogous to the diminution of the vapour-tension of mixed liquids, which is usually less than the sum of the separate tensions. Take, for example, the case of iodine in presence of water and carbon bisulphide. 10 c.c. of carbon bisulphide saturated with iodine at 18° contain 1.85 gram of iodine; and 10 c.c. of water at the same temperature can take up 0.014 gram iodine. The ratio of these two solubilities is 1 : 132. On the other hand, when carbon bisulphide nearly saturated with iodine is shaken up with water at 18°, 10 c.c. of the carbon bisulphide retain 1.74 iodine, and 10 c.c. of the water take up 0.0042 iodine. Now the ratio of these numbers is 1 : 410, that is to say, the coefficient of division is only about one-third as great as the ratio of the solubilities. In like manner, for succinic acid in presence of water and ether, the ratio of the solubilities from saturated solution is 10<sup>4</sup>, whereas the coefficient of division for the same degree of concentration is only 6.8.

The same holds good when the soluble body dissolves to a finite extent only in one of the liquids, but is capable of mixing in all proportions with the other. Take, for example, the case of bromine in water and carbon bisulphide: here, as already determined (p. 283), the coefficient of division is about 1 : 80; but the ratio of the solubilities is infinite.

5. With regard to the relations between the coefficient of division and the chemical composition of the substance dissolved, it is found that ether removes from water with comparatively greater facility—

a. The more highly carburetted of two homologous acids, *e.g.*, succinic more easily than oxalic acid; butyric more easily than acetic acid.  $\beta$ . A monobasic in preference to the corresponding bibasic acid; *e.g.* acetic rather than oxalic, butyric rather than succinic acid.  $\gamma$ . A monobasic acid rather than a bibasic acid of nearly the same centesimal composition; *e.g.* acetic rather than succinic acid.  $\delta$ . Of two acids containing the same proportion of carbon and hydrogen, the less oxygenated is the more easily removed; *e.g.* succinic acid  $C^4H^6O^4$  rather than malic  $C^4H^6O^5$ , malic rather than tartaric  $C^4H^6O^7$ .

6. Two bodies placed simultaneously in contact with two solvents are distributed between them just as if each of the bodies acted alone. This law, which has been verified by Berthelot in the action of water and ether on various mixtures of acetic and tartaric, of acetic and oxalic, and of oxalic and tartaric acid, is analogous to the law of solubility of mixed gases.

**State of Salts in Solution** (Berthelot a. St. Martin, *Ann. Chim. Phys.* [4] xxvi. 433). The method of experimenting above described is applicable to the determination of the state of acid salts in solution, and to the question of the division of a base between two acids in solution.

I. To determine the state of an acid salt in solution, a measured volume of the solution, of known strength, is agitated with a known volume of ether. Three cases may occur: a. The water completely decomposes the acid salt into neutral salt and free acid. In this case the solution will yield to the ether a quantity of acid equal to that which the ether, under similar circumstances, would take from a solution of the free acid of the same strength.  $\beta$ . The water partially decomposes the acid salt, so that the solution contains a mixture of acid salt, neutral salt, and free acid; in this case the quantity of free acid removed by the ether will afford the means of calculating by means of the division coefficient, the quantity of acid which existed in the solution in the free state before the agitation.  $\gamma$ . The water exerts no action on the acid salt. In this case the ether, both before and after agitation, remains perfectly neutral to litmus.

As the coefficient of division between water and ether varies with the temperature and with the concentration of the aqueous liquid, it is necessary to make a comparative experiment with the acid of the salt which is the subject of experiment. For this purpose, a solution of the free acid is prepared of the same acidimetric strength as that of the acid salt; and the coefficient of division between this solution and the ether is determined, using volumes of these liquids exactly equal to those which were employed in experimenting on the acid salt, the two experiments being made simultaneously, so that the conditions of temperature may be the same.

When the acid salt is completely resolved into neutral salt and free acid, the two experiments will give the same result; in the contrary case, the acid salt will yield a smaller proportion of free acid; and by a series of trials, the particular solution of free acid may be found which yields to ether the same proportion of the acid as the acid salt. In all cases, if the liquid is dilute, the proportion of free acid in the solution of the acid salt may be calculated from the quantity found for the solution of free acid. Supposing that the quantities of free acid yielded to the ether by the two solutions are proportional to the quantities which remain dissolved in them, the sum of the two quantities dissolved by the water and the ether after agitation will give the quantity of pre-existing acid. This calculation supposes that the coefficient of division is constant, which is sensibly true for dilute liquids (p. 283).

The principal results obtained by this mode of experimenting are the following:—

1. Acid salts of monobasic acids, such as the biacetate and bibenzoate of potassium, cannot exist in dilute aqueous solution, but are immediately broken up into neutral salt and free acid. From a solution of sodium biacetate, for example, ether dissolves out a portion of the free acid, but not the sodium acetate or biacetate. Moreover, the coefficient of division is exactly the same as that of a solution of acetic acid of the same degree of acidity.

2. Acid salts of polybasic acids, on the contrary, can exist in solution, but generally in a state of partial decomposition. Such is the case with the bioxalates, bitartrates and especially the bisuccinates of potassium and ammonium, which last salts are more

soluble in water than those of the other two classes, and contain an acid more soluble in ether. Potassium quadroxalate splits up on solution into the bioxalate and free oxalic acid. All these acid salts are as insoluble in ether as the corresponding neutral salts.

3. *The quantity of salt decomposed increases slowly and continuously with the degree of dilution.*

4. *The quantity decomposed likewise changes continuously with the proportion between neutral salt and excess of acid present, in such a manner that the stability of the acid salt is increased by the presence of an excess, either of neutral salt or of free acid, the increase of stability being quicker however in the latter case than in the former.*

*Division of a Base between two Acids.*—Experiments on this division were made by adding to the aqueous solution of the neutral salt of an acid which is dissolved out by ether from its aqueous solution in considerable quantity, another acid whose coefficient of division is very different from that of the former acid. The whole was then agitated with ether, and the final condition of the two liquids determined. At the same time, two other liquids of the same acid strength, each of them however, containing only one of the two acids, were treated in a similar manner.

By a series of experiments thus made on solutions of sodium acetate with dilute solutions of hydrochloric, sulphuric, oxalic, and tartaric acids, it was found that each of these acids is able completely to displace the acid of the acetate from its bases. Reciprocal experiments, in which acetic acid was added to the solutions of sodium chloride, sulphate, oxalate, and tartrate, confirmed this result.

It was proved also that ammonia has no power to displace the alkali-metals from their acetates and oxalates.

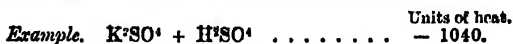
By adding oxalic acid solution to a sufficiently dilute solution of common salt, it was found that about  $\frac{1}{10}$ th of the oxalic acid was converted into sodium bioxalate, about 5 p. c. of the sodium being removed from its combination with the chlorine.

The results obtained by the preceding methods are corroborated by the thermic phenomena exhibited in the solution of salts in water and in the mutual action of acids and metallic salts. On this subject numerous experiments have been made by Berthelot. In one series (*Compt. rend.* lxxv, 207 and 263), the reactions of salts of potassium, sodium and ammonium with hydrochloric and nitric acids were examined. The strength of the solutions was such that two litres contained an equivalent of the salt in grams. Similar solutions of the two acids were made. With the solution of each salt was mixed an equal volume of the acid proper to it, and the change of temperature was observed. In these cases the heat absorbed or disengaged was barely perceptible, and scarcely greater than that allowed for experimental errors.

Thus for the salts of potassium:



Similar experiments were tried with the sulphates of the alkali-metals and oxalic acid, in a solution, whose strength was half an equivalent in grams to two litres of water.



On mixing the solution of the other salts with the acid solution, similar quantities of heat were absorbed. Such figures indicate a decided reaction between the neutral and the acid salt.

To examine the nature of this reaction, different quantities of acid solution were successively added to solutions of potassium sulphate, and the heat absorbed was observed. Thus there were in solution successively  $\text{K}^2\text{SO}^4 + \text{H}^2\text{SO}^4$ ,  $\text{K}^2\text{SO}^4 + 2\text{H}^2\text{SO}^4$ , &c. . . . .  $\text{K}^2\text{SO}^4 + 10\text{H}^2\text{SO}^4$ ; and it was found that the quantity of heat absorbed became greater as the quantity of acid added was greater, but that it had a limiting value, about 2,000 units of heat, a quantity which may be looked upon, as that which represents a complete transformation of the neutral into the acid sulphate. Similar results were obtained with oxalate of sodium.

Again experiments were made by adding to solutions containing one equivalent of sulphuric acid, one, two, or more equivalents of neutral potassium sulphate. The result was similar to that just described, reactions being obtained which approached more and more closely to that which would correspond with complete conversion of the sulphuric acid into the acid sulphate of potassium. Oxalic acid gave a similar result with neutral oxalate of sodium. The limiting value for the quantity of heat absorbed in these last experiments—a value which may be supposed to belong to a complete

\* The unit of heat is the quantity of heat required to raise 1 gram of water 1° C.

conversion of an equivalent of sulphuric acid into acid sulphate of potassium by the action of a large quantity of neutral sulphate, or of an equivalent of oxalic acid into acid oxalate of sodium by means of neutral oxalate—was the same as that found for the converse reaction, being 2,000 units of heat for the sulphate of potassium, and 600 units for the oxalate of sodium; and it is interesting and important to remark that the heat given out during the conversion by means of potash, of sulphuric acid into potassium sulphate, viz., 15,700 units, when reduced by this number 2,000, gives 13,700 units, the same quantity that is given out during the conversion of a monobasic acid, such as nitric or hydrochloric acid by the same means. A similar comparison may be made for the case of sodium oxalate.

Lastly, experiments were tried as to the effect of the water of solution, and it was found that, on mixing an equivalent of sulphuric acid with an equivalent of neutral potassium sulphate, each in the first instance dissolved in one litre of water, then each in two, afterwards each in five litres, and so on, the quantity of heat absorbed became less and less. This represents a reaction less and less complete as the solution is more and more dilute. In a solution in which one equivalent of the acid salt is contained in 20 litres of water, little more than the half will remain as an acid salt, the remainder being split up into free acid and neutral sulphate.

These facts concur in showing that there is a species of equilibrium, by means of which, in the case of the salt of a bibasic acid, the four bodies, the water, the acid salt, the free acid, and the neutral salt, all coexist in the same solution. The proportion in which they coexist depends upon the proportions of water, acid, and neutral salt present.

The formation of an acid sulphate by solution is accompanied by an absorption of heat, which however is only apparent, the actual formation of the acid salt being attended with a development of heat, and the fall of temperature observed being due to secondary phenomena connected with the solution of the salt in water, which, taken together, overpower the effect due to the formation of the salt.

In the case of monobasic acids, the experiments were made as follow:

Solution of sodium acetate—one equivalent in grams dissolved in two litres of water—was mixed with aqueous nitric acid, 1 eq. in 2 litres, and the quantity of heat given out during the mixing was determined. Next, solution of sodium nitrate, 1 eq. in 2 litres, was mixed with acetic acid solution of the same strength, and the heat given out was observed. The quantity of heat found as the representative of the chemical combination which takes place was, for the first operation, +450 units, and for the second, -60; the total, found by subtracting the second from the first, that is, by adding 60, is 510 units. Comparing this with the difference between the heats developed during the neutralisation of weak nitric acid and of weak acetic acid with soda, the number is found to be exactly the same, and in favour of the nitric acid combination. Hence it is concluded that when nitric acid and acetic acid in equivalent quantities are present in the same solution and in presence of one equivalent of soda, the nitric acid takes the whole of the soda to itself, and the acetic acid remains completely uncombined.

Hydrochloric acid, in presence of acetic acid and soda, likewise completely satisfies itself by forming sodium chloride, as proved by the heat evolved. The phenomena observed when a bibasic acid and a monobasic acid are together presented to a single base in solution are various, and such is the case when two bibasic acids are simultaneously presented to the same base. Carbonic acid is completely displaced from its combination by nitric, acetic, sulphuric, and tartaric acid, no bicarbonate being formed. Sulphuric acid completely displaces acetic acid from its combination with the alkalis, and during the reaction much heat is given out. Tartaric acid almost completely displaces acetic acid, but during the reaction heat is absorbed. The result is confirmed by the method of two solvents, above described, which shows complete conversion of acetates into tartrates.

The reactions of the oxalates and sulphates in presence of nitric and hydrochloric acids are more complex than those mentioned above. Here it is found that acid salts are formed in quantity depending on the amounts of the various bodies present. The quantity of water especially has an important influence on the result. As already pointed out, the six bodies in the solution form a kind of equilibrium among themselves. For example, the result of the finished reaction, and consequently the amount of heat given out, depends on the equilibrium due to the quantities formed of sodium sulphate, sodium bisulphate, free sulphuric acid, sodium nitrate, free nitric acid, and water.

The following experiments relate to the formation of metallic salts by the union of acids with the oxides of zinc, copper, lead, &c., and particularly of ferric oxide, (Berthelot, *Compt. rend.* lxxiii. 1472; lxxiv. 48 and 119).

In the case of many of the salts of these metals, the concentration of the solution

exerts a far greater influence on the quantity of heat disengaged during a reaction than it does in the case of salts of the alkalis. Thus equivalent quantities of—

	Heat-units.
Zinc acetate (1 eq. in grams in 10 litres) and caustic potash (1 eq. in 2 litres) being mixed, gave	+ 4400
Zinc acetate (1 eq. in 2 litres) and caustic potash (1 eq. in 10 litres).	+ 540

This effect is almost entirely due to the difference in concentration of the zinc acetate: for if a solution of caustic potash, one equivalent in two litres, be diluted with water so as to become ten litres, the thermal effect is scarcely appreciable, neither is the effect of the dilution of an alkaline acetate more perceptible. On the other hand, solution of zinc acetate, 1 equivalent in 2 litres,

diluted to 4 litres, gives 500 heat-units.

" 10 " 101 "

The heat developed during the solution of zinc oxide in acetic acid in presence of different quantities of water, increases as the solution is diluted; and the same is the case with many other salts. In some cases, however, as in those of the acetates of potassium and sodium, and in that of zinc sulphate, the addition of water has little or no effect after a certain point is reached.

Experiments were also made to ascertain, by observation of the heat developed or mixing solutions of various salts, when double decomposition takes place. Thus zinc acetate was mixed with sodium sulphate, and zinc sulphate with sodium acetate, and it was found that, in the former case, the heat given out is nothing more than that due to the dilution of the zinc acetate, while in the latter the occurrence of double decomposition must be supposed, in order to account for its development or absorption. It is thus shown that, on mixing two solutions of salts, the final result is that the stronger base unites with the stronger acid, and the weaker base with the weaker acid; in fact that salts are formed in the order of their stability, double decomposition occurring when necessary for this final result. This was shown to hold for the various salts of several metals, but the most striking results were obtained in the case of the ferric salts.

Ferric sulphate, nitrate, and acetate were examined, each salt first by itself in solutions of varied concentration, then in mixture with solutions of other salts, with the view of determining, by means of the heat given out during dilution and mixture, the state of the union existing between the acid and base. The instability, or at least the feebleness, of the union was first pointed out by Péan de St. Gilles in the case of the acetate. Solutions of the salts: first, recently dissolved; secondly, recently dissolved, but boiled for some minutes and then cooled; and, thirdly, after the solution had been kept for three months,—were mixed with equivalent solutions of caustic potash, and the following results were obtained:—In the case of the sulphate, the heat developed in all three cases is nearly the same; but in the case of the nitrate, while the solution of the salt recently dissolved in the cold is sensibly unchanged by boiling, the same solution kept for three months gives a result which proves that slow disunion between the base and the acid has been going on. The acetate is also found to be slightly decomposed when the solution is kept for a long time, but when it is boiled for a few minutes, the acid and base are found to be almost completely disunited.

When a solution of ferric acetate is boiled and then mixed with solution of potassium sulphate, a secondary disengagement of heat takes place, indicating a molecular coagulation or condensation, which appears to correspond with the assumption of the insoluble state in which the oxide is found after this kind of precipitation.

The general results of the investigation are that, in solutions of ferric salts, the oxide and the acid are united in an incomplete and feeble manner, and the union is affected by the water of the solution, and greatly by temperature: this is most apparent in the case of salts formed with the weaker acids. The reaction of the water in breaking up the salt is not instantaneous, but progressive, as is the case with the decomposition of ethers by water; and finally the effects are not always reversible by reversing the conditions: for the oxide of iron once separated from its acid assumes a molecular condition which prevents it from returning to its old state in combination.

In the action of an acid on its corresponding ferric salt, heat is liberated, in the case of the nitrate and sulphate, when the acid solution is added, which indicates an increased union between the oxide and the acid, due to the presence of free acid. A solution of an alkaline salt of the same acid does not produce much



effect on the solution of the ferric nitrate or sulphate, but when solution of sodium acetate is mixed with solution of ferric acetate, complete though gradual decomposition takes place.

The presence of two ferric salts in a solution diminishes the decomposing power of water on each of them.

When a solution containing an equivalent of nitric acid is mixed with a solution containing an equivalent of ferric sulphate or ferric acetate, the sulphuric acid or the acetic acid is displaced by the nitric acid. Sulphuric acid completely displaces acetic acid from ferric acetate.

Finally, the double decompositions which take place on adding solutions containing various salts in equivalent quantities to solutions of ferric salts confirm the rule, that the stronger acid joins itself to the stronger base.

**Ammonia Salts.**—By observations on the heat developed in the combination of ammonia with strong and weak acids in presence of various proportions of water, Berthelot finds that, in the case of strong acids, the results are not sensibly affected either by different degrees of dilution or by the presence of excess of ammonia or of the acid, but that with weak acids, as phosnic, boric and carbonic, the proportion of acid, base, and water exercises a very decided influence on the quantity of heat developed; thus, in the formation of ammonium borate in presence of quantities of water varying from 220 to 1320 eq. the heat evolved varies from 2250 to 3640 units; and in the formation of the carbonates of ammonium, the quantities of heat evolved vary with the proportions of carbonic anhydride, ammonia and water, in the manner shown in the following table:—

CO <sup>2</sup> +	NH <sup>3</sup> in presence of 110H <sup>2</sup> O disengages	9730
+ 1½ NH <sup>3</sup>	" "	146H <sup>2</sup> O " 10940
+ 2 NH <sup>3</sup>	" "	220H <sup>2</sup> O " 12340
+ 3 NH <sup>3</sup>	" "	330H <sup>2</sup> O " 13240
+ 4 NH <sup>3</sup>	" "	440H <sup>2</sup> O " 13620
+ 5 NH <sup>3</sup>	" "	550H <sup>2</sup> O " 13920
+ 6 NH <sup>3</sup>	" "	660H <sup>2</sup> O " 14040
+ 7 NH <sup>3</sup>	" "	770H <sup>2</sup> O " 14070

These results show that the proportion of water present exercises a much more marked influence on boric acid than on carbonic acid, but that the decomposing influence of water seems to produce, at first, greater effects on the compounds of the latter, which however rapidly becomes very small, whilst with boric acid the progression is more regular (*Compt. rend.* lxxiii. 864).

The opinion generally entertained that no thermal effects are produced by mixing neutral salts is not justified by the behaviour of salts with weak acids. Whilst the carbonates of potassium and sodium and the bicarbonate of ammonium are not only not decomposed by water, but do not evolve any heat when mixed with neutral salts of the alkalis, the neutral carbonates of the fixed alkalis absorb heat on being brought together with the neutral ammonium carbonate, and liberate heat with the bicarbonate of ammonium. Neutral ammonium carbonate mixed with potassium or sodium carbonate liberates heat.

Ammonium bicarbonate is decomposed by the carbonates of potassium and sodium, heat being absorbed, whilst it evolves heat when mixed with neutral ammonium carbonate.

Ammonia alone does not produce any reaction with potassium carbonate.

These facts can only be explained on the supposition that neutral ammonium carbonate does not exist as such in its aqueous solution, but that part of it splits up into bicarbonate and free ammonia. If, then, potassium bicarbonate be present, it is neutralised by the ammonia. The action of the ammonium bicarbonate upon the neutral potassium salt must be regarded as a double decomposition, inasmuch as potassium bicarbonate is formed, together with neutral ammonium carbonate, which again splits up in the manner already described. Whatever the original state of things may have been, the final equilibrium arrived at is always the same, giving rise simultaneously to five compounds, viz., the neutral carbonate of potassium (or sodium) and ammonium, the bicarbonates of the same bases, and free ammonia.

Bicarbonate of ammonium does not show any thermic reactions when brought into contact with the neutral salts (chloride, nitrate, sulphate, &c.) or with the bicarbonates, of potassium and sodium; moreover the difference of the heats of combination of the bicarbonates of potassium and ammonium is the same as the difference of the heats of combination of the potassium and ammonium salts with strong acids: hence it appears that ammonium bicarbonate in presence of water is quite as stable as the bicarbonate of potassium and sodium.

From this it may be inferred that it is not the gaseous tension of ammonia and carbonic acid exhibited in the solid ammonium carbonates which causes these salts in their aqueous solution to change their states of equilibrium.

In general, it appears that any system formed by a mixture of ammonia, carbonic acid, and water, always tends to the same state of equilibrium, whatever its original conditions may have been. When the original state of combination is less advanced than that required for the existence of equilibrium, heat will be evolved, whereas it is absorbed when the original state of combination is more advanced than that corresponding to the state of equilibrium.

It is this state of incomplete combination, that is to say, the manner in which the base of a salt divides itself between acid and water, which characterises the weak acids, and may in future enable us to define more precisely than before the vague terms *weak and strong acids and bases*.

The neutral salts formed by *strong acids* are stable, inasmuch as the addition of water or an excess of base does not give rise to any decomposition or other reaction indicated by the thermometer. *Weak acids*, on the other hand, form with most of the strong bases, and especially with ammonia, salts capable of being decomposed by water (Berthelot, *Compt. rend.* lxxiii. 951, 1003).

The thermal phenomena produced when two salts are mixed in solution indicate generally that the strong acids combine by preference with the strong bases, leaving the weak acids to combine with the weak bases, so that the salt most stable in the presence of water, and as a necessary consequence the one least stable, are formed.

1st. *Both salts formed with Strong Acids.*—When solutions of two neutral and stable salts are mixed, a feeble thermal effect is produced, which is not the sum of the effects produced by pure water on the two solutions separately, taken at the same temperature.

2nd. *One salt formed with a Strong, and one with a Weak Acid.*—Experiments on the action of the neutral carbonates, bicarbonates, phenates, borates, cyanides and sulphhydrates of the alkali-metals on ammonia salts have shown that the potash or soda always combines with the stronger acid, leaving the ammonia to combine with the weaker. If the ammonium salt formed is stable in presence of water, the thermal effects produced by the mixing are but slight; if, on the other hand, the ammonium salt produced is decomposed by water, as the carbonate for example, an appreciable absorption of heat is the result.

These facts, together with others observed in the reaction of salts both containing weak acids, show that double decomposition takes place between salts in solution, by which the compound most stable under the conditions of the experiments is always formed chiefly, if not exclusively.

The various conditions of equilibrium thus developed play an important part in cases where some of the salts are precipitated as well as in those in which they all remain dissolved (Berthelot, *Comp. rend.* lxxii. 1050).

**Precipitation.** In the formation of precipitates there is for the most part a development of heat, just as in the solidification of a melted substance; but in the former case the operation is much more complicated, as various other actions have to be considered, such as crystallisation, change of aggregation, &c.

1. *Formation of a Solid Compound.*—The heat disengaged in the formation of a precipitate is due in great part to the separation of a solid body, as is shown by an examination of those salts which produce precipitates only when the solutions are concentrated, such as lead chlorido, potassium picrate, and calcium tartrate. *Lead Chloride.*—On adding a dilute solution of sodium chloride to one of lead nitrate, so that no precipitate is formed, an absorption of heat takes place, about equal to that produced by the dilution of the lead solution; but when a precipitate is formed, there is a disengagement of + 2000 heat-units for each equivalent of lead chloride actually precipitated. *Potassium Picrate.*—If dilute solutions of potash and picric acid be mixed, the heat disengaged corresponds to that of neutralisation, but when a precipitate is obtained, + 10,000 heat-units are disengaged for each equivalent of salt precipitated. *Calcium Tartrate.*—Solutions of sodium tartrate and calcium chloride remain limpid when first mixed, heat being at the same time disengaged (+ 1040). After the lapse of some minutes, however, a crystalline precipitate of calcium tartrate is formed, accompanied by a further disengagement of heat (+ 2060). From each of these examples it may be seen that it is not the chemical reaction which causes the chief disengagement of heat; but it must not be imagined that all precipitation is attended with evolution of heat, as the effects of dehydration, &c., sometimes render it even negative.

2. *Dehydration of the Compounds Precipitated.*—Lime. Andrews has observed that the precipitation of lime from dilute solutions by potash gives rise to an absorption of

heat, which may be explained by the fact that calcium hydrate dissolves in water with disengagement of heat, so that the precipitation of lime should be accompanied by a dehydration, that is a decomposition, the heat absorbed by which more than compensates for that which is disengaged during the solidification of the calcium hydrate. *Calcium carbonate* also precipitated in an amorphous form gives rise to an absorption of heat, which Bertholot believes to be due to the partial dehydration of the compound at the moment of its precipitation. *Magnesium carbonate*, *ferrous carbonate*, and *manganese carbonate* give rise to an absorption of heat, representing a dehydration of the insoluble compound. *Calcium sulphate* and *strontium sulphate*.—The mixed solutions of sodium sulphate and calcium or strontium chloride remain clear, a slight absorption of heat taking place; on causing precipitation, however, by the introduction of some crystals of the sulphate, there is a slight disengagement of heat. *Barium sulphate*, when precipitated, on the contrary, evolves considerable heat (+ 2500 to + 2900). These results indicate the existence of a thermic action of a contrary sign to that of solidification, and varying in the different salts.

3. *Separation of the Acid and Base in Salts*.—Not only can the saline hydrates which exist in solution be transformed into precipitated hydrates of a different type by double decomposition, but even a partial or total separation between the acid and base may be effected, in which case, as in that of dehydration, heat is absorbed. In general this decomposition is not complete, the normal compound being separated into two others, a basic hydrated salt, which is precipitated, and an acid salt which remains dissolved. *Zinc Carbonate*.—The composition of this precipitate varies according to the temperature and the proportions of water, base and carbonic acid which are present, and its formation is attended with absorption of heat. In the normal reaction, when equivalent quantities are used, the total absorption of heat does not take place at once, a secondary reaction setting in by which a further but comparatively small amount is absorbed. These phenomena correspond with the formation of a basic hydrocarbonate mixed with double salts of variable composition. If an alkaline bicarbonate be substituted for the carbonate, neutral zinc carbonate is precipitated, the heat absorbed in this case being much less than with the alkaline carbonates. This reaction also takes place by two stages, and after a time a third action commences, accompanied by an absorption of heat, and a very feeble evolution of gas. This is due to the formation of zinc bicarbonate, which subsequently undergoes decomposition, neutral zinc carbonate (mixed with a double salt) being precipitated, and carbonic acid remaining in solution. The absorption of heat is more feeble than with the neutral alkaline carbonates, as it represents only the decomposition of the zinc bicarbonate into neutral carbonate and carbonic acid. *Copper carbonate*, precipitated by an alkaline carbonate, produces in strong solutions (1 equiv. = 2 lit.) an absorption of heat, which, like the precipitation, is immediate; after a short time effervescence sets in with further cooling, indicating that normal cupric carbonate has but an ephemeral existence. *Ferric carbonates*.—On treating crystalline ferric nitrate with potash, 7870 heat-units were disengaged, from which it may be calculated that ferric nitrate (1 equiv. = 2 lit.) poured into potassium carbonate (1 equiv. = 2 lit.) would absorb -100. From the results obtained with ferric sulphate and iron-alum, it may be inferred that no definite ferric carbonate is formed, but divers complex systems containing a basic salt, an acid salt, and free acid. *Alumina*.—From the results of treating aluminium sulphate with potassium carbonate, it would appear that a molecular condensation of the alumina takes place. *Chromium*.—With chrome-alum and an alkaline carbonate there is, at first, an absorption of heat, and afterwards a feeble effervescence, accompanied by a disengagement of heat, indicating that there is a special molecular change in the chromium oxide comparable with the formation of a polymeric body.

4. *Changes in the State of Aggregation*.—This is the case with those precipitates which are amorphous in the first instance, but gradually aggregate and finally become crystalline; these successive changes, which may be observed under a microscope, give rise to an evolution of heat. *Strontium carbonate* is precipitated in an amorphous state, accompanied by absorption of heat (-400), but the precipitate after a time becomes crystalline, causing an evolution of heat + 400 to + 560. With *barium carbonate* the difference between the two actions is less marked. *Lead carbonate* at first disengages + 400, but the thermometer mounts rapidly, and ultimately the amount of heat disengaged is 2620. In *silver carbonate* the thermic results correspond with amorphous states which succeed one another too rapidly to be distinguished. From results obtained with dilute solutions, however, it is calculated that the heat evolved in the combination of carbonic acid and hydrated silver oxide exceeds that of the formation of silver nitrate. The precipitation of the *oxalates*, which are for the most part crystalline, disengages much heat, the calcium salt evolving as much as barium sulphate.

Many effects marked by thermic phenomena are produced during the double decomposition of salts; at the moment when the solutions are mixed, a certain definite equilibrium is attained, depending upon the proportions of water, of the primitive salts, and of those newly formed; but when these latter are insoluble, they undergo further changes both chemical and physical, such as dehydration, crystallisation, &c. The heat disengaged, therefore, is not the measure of the forces set in action, except in those cases where each individual change causes an evolution of heat, or the contrary.

**Decomposition of Crystalline Salts in Solution.**—*Crystalline Dissociation* (Favre a. Valson, *Compt. rend.* lxxiii. 1144; lxxiv. 1016, 1065; lxxv. 798, 925, 1000, 1066, 1071. *Gazzetta chimica italiana*, ii. 100, 563, 569. *Chem. Centr.* 1872, 26, 457, 475, 572, 651, 730; 1873, 42. *Chem. Soc. J.* [2] x. 22, 600, 1068; xi. 32, 129). When a crystalline salt is dissolved in water, a variety of phenomena take place. In the case of a crystal of sodium sulphate ( $\text{NaSO}_4 + 10\text{HO}$ )\* for instance, it may be conceived, in the first place, that there is a disaggregation of the molecules which compose the crystalline edifice, and that, moreover, there is an effect analogous to fusion. The latter is probably of a complex nature, being accompanied (1) by the disunion of the chemical molecules, and (2) by the separation of the water associated with the salt to form the crystal, or by the addition of more water to it. The quantitative chemical methods hitherto applied to the solution of this problem do not enable us to distinguish between the separate amounts of work of which the final result is made up. It is better, therefore, to resort to thermochemical methods; but, even then, serious difficulties present themselves: for, although the combination of molecules gives heat, and their separation produces cold, still the final result represents only the difference between these two, and in the present state of science this difficulty cannot be directly resolved.†

The sulphates have many advantages for this investigation, as they differ considerably in their crystalline form; and while some are anhydrous and others contain more or less water of crystallisation, many of them, being isomorphous, are capable of crystallising together. These salts have been examined in the crystalline state, either anhydrous or containing more or less water of crystallisation, and in the state of salts partially dehydrated by heat or by treatment with alcohol. Table I. contains the results obtained with salts of various degrees of hydration; Table II. those given by isomorphous salts crystallised together:—

TABLE I.

Substance	Heat-units	Substance	Heat-units
$\text{FeSO}_4 \cdot 7\text{HO}$ . . . .	— 2182	$\text{MgSO}_4 \cdot \text{HO}$ . . . .	5493
$\text{ZnSO}_4 \cdot 7\text{HO}$ . . . .	— 2074	$\text{CuSO}_4 \cdot \text{HO}$ . . . .	4734
$\text{MgSO}_4 \cdot 7\text{HO}$ . . . .	— 1860	$\text{MnSO}_4 \cdot \text{HO}$ . . . .	4216
$\text{NiSO}_4 \cdot 7\text{HO}$ . . . .	— 1944	$\text{CdSO}_4 \cdot \text{HO}$ . . . .	3010
$\text{CoSO}_4 \cdot 7\text{HO}$ . . . .	— 1680	$\text{MgSO}_4$ . . . . .	10152
$\text{CuSO}_4 \cdot 5\text{HO}$ . . . .	— 1216	$\text{ZnSO}_4$ . . . . .	9289
$\text{MnSO}_4 \cdot 5\text{HO}$ . . . .	+ 235	$\text{CuSO}_4$ . . . . .	8149
$\text{CdSO}_4 \cdot 3\text{HO}$ . . . .	+ 1531	$\text{MnSO}_4$ . . . . .	7085
$\text{NaSO}_4 \cdot 10\text{HO}$ . . . .	— 9300	$\text{CdSO}_4$ . . . . .	5344
$\text{ZnSO}_4 \cdot \text{HO}$ . . . .	+ 4812	$\text{NaSO}_4$ . . . . .	354
$\text{ZnSO}_4 \cdot 3 \cdot 75\text{HO}$ . . . .	+ 2205	$\text{KSO}_4$ . . . . .	— 3170
$\text{ZnSO}_4 \cdot 4 \cdot 46\text{HO}$ . . . .	+ 1354	$(\text{NH}_4)\text{SO}_4$ . . . .	— 975
$\text{ZnSO}_4 \cdot 4 \cdot 55\text{HO}$ . . . .	+ 1198		
$\text{ZnSO}_4 \cdot 6 \cdot 17\text{HO}$ . . . .	— 397		

\* O = 8; S = 16.

† This problem resembles that of simultaneous equations of several unknown quantities in algebra requiring, in order to solve it, as many independent equations as there are unknown quantities.

TABLE II.

Substance	Heat-units	The crystals contain
Copper sulphate and zinc sulphate crystallised together		
ZnSO <sup>4</sup> .5HO : : : .	— 1166	23.28 p. c. ZnSO <sup>4</sup> .5HO
CuSO <sup>4</sup> .7HO : : : .	— 2060	44.30 p. c. CuSO <sup>4</sup> .7HO
Copper sulphate and magnesium sulphate crystallised together		
MgSO <sup>4</sup> .5HO : : : .	— 1194	10.94 p. c. MgSO <sup>4</sup> .5HO
CuSO <sup>4</sup> .7HO : : : .	— 2130	47.37 p. c. CuSO <sup>4</sup> .7HO

It will be observed that the anhydrous sulphates give very different numbers, although they are mostly positive, and that this difference disappears as the number of equivalents of water in the crystal increases. Hence it appears that the greater part of the heat evolved during the solution of an anhydrous salt, or of a salt in a state of hydration inferior to its normal state, is due to the formation of the crystal which contains the normal proportion of water. Moreover, the heat due to the combination of the first molecule of water, greatly exceeds that due to the succeeding molecules: thus between anhydrous magnesium sulphate and the same with one equivalent of water, there is a difference of 4659 heat-units for the addition of one equivalent of water, whilst between magnesium sulphate with five and that with seven equivalents, there is only a difference of 666 for two equivalents of water.

Another question now arises as to what is the state of a salt partly dehydrated by alcohol? It will be found, by interpolation of the numbers in Table I., that the number of heat-units corresponding to zinc sulphate dehydrated by alcohol and containing five equivalents of water, is 1000, whilst zinc sulphate with five of water, obtained by crystallisation with copper sulphate, gives — 1166, being a difference of 2166 heat-units.

Again, with regard to double salts, it is found by experiment that the amount of heat set free by the solution of one of two salts remains sensibly the same, even if the water already contains the other salt in solution, so that if two salts are dissolved in water, the total amount of heat is the same as the sum of the two determined separately. If, however, they exist crystallised together as a double salt, they give a very different result:—

TABLE III.

Substance	Heat-units	A. Sum	Substance	D. Heat-units	Difference between A and B
KSO <sup>4</sup> . . .	— 3170	— 4386	Double salt, with 7HO	— 7180	2794
CuSO <sup>4</sup> .5HO . .	— 1216				
(NH <sup>4</sup> )SO <sup>4</sup> . . .	— 975	— 2191	Double salt, with 7HO	— 5622	2431
CuSO <sup>4</sup> .5HO . .	— 1216				
KCl . . .	— 4574	— 2251	Double salt, with 2HO	— 3491	1241
CuCl.2HO . .	+ 2323				

It will be seen from this table that the amount of cold produced by double salts in dissolving is much greater than the sum of the amounts produced by the two salts dissolved separately. This effect appears to be due to the fact that a certain amount of work is done in the formation of a double salt, giving rise to a disengagement of heat, and that when the double salt is dissolved, there is an inverse work of decomposition, characterised by cold; according to this supposition, the numbers in the column of differences represent the work of combination or decomposition. Experiment also seems to establish a relation between the heat disengaged and the contraction which takes place when a salt is dissolved. If the density  $d$ , of an anhydrous salt is known, the volume  $V$ , occupied by an equivalent  $p$ , can be deduced from it. When this equivalent is dissolved, say in a litre of water, it is easy to determine the increase of volume  $v$ . The difference  $V - v$  represents then the contraction of the salt on being

dissolved, whilst  $\frac{V-v}{V}$  will represent the *coefficient of contraction* with respect to the original volume  $V$ .

The values of  $d$  in the following table are those given by Filhol; the values of  $v$  are deduced by methods which will be described further on (p. 298):

TABLE IV.

Anhydrous salts	$p$	$d$	$V = \frac{p}{d}$	$v$	$V-v$	$\frac{V-v}{V}$	$c$
KSO <sup>4</sup> . . .	87 gr.	2.6	33	21	12	0.36	— 3170
NaSO <sup>4</sup> . . .	71	2.6	27	10	17	0.63	354
CuSO <sup>4</sup> . . .	80	3.5	22	4	18	0.81	8149
ZnSO <sup>4</sup> . . .	80.75	3.4	23	4	19	0.83	9289
MgSO <sup>4</sup> . . .	60.50	2.6	23	3	20	0.87	10152

In this table  $c$  is the number of heat-units, and it will be seen that they increase in the same ratio as the contraction  $V-v$ , or the coefficient of contraction  $\frac{V-v}{V}$ ; from this it would appear that the heat disengaged increases with the contraction effected in the substance, and is, at least partly, the immediate consequence of it.

From the general principle that the different forces necessary to produce a given effect are equivalent to one another, it follows that the contractions produced in a liquid: (1) by lowering the temperature, (2) by external compression, (3) by the solution of a salt, may be considered as three effects of the same order, and consequently equivalent to the forces which produce them. From the known coefficient of the expansion of water (0.0001320 according to Kopp) it follows that a litre of water, when cooled 1°, contracts to 9,998,680 c. c. and that a contraction of 1 c. c. per litre corresponds with a fall of temperature equal to 7.576°, i.e. to 75.76 units of heat. This number is therefore the measure of the work required to compress a litre of water by 1 c. c. at 15°. On the other hand, Regnault has shown that the coefficient of compression of water = 0.00004685, for one atmosphere: consequently the compression of a litre of water by 1 c. c. requires a force of 20.34 atmospheres. From this it may be inferred that a litre of water subjected to a compression of 21.34 atmospheres would disengage 7576 units of heat.

If then we suppose a salt to be dissolved in a litre of water in quantity sufficient to produce a contraction of 1 c. c. it follows that the sum of the forces which come into play, whatever may be their mode of distribution, is equivalent to 7576 units of heat, or to a pressure of 21.34 atmospheres.

For sodium sulphate the following numbers have been obtained:

Anhydrous salt (Equivalent),	. . . . .	$P = 71$ grams
" " (Density) . . . . .	. . . . .	$D = 2.681$
" " (Volume) . . . . .	. . . . .	$V = \frac{P}{D} = 26.5$ c. c.
Hydrated salt with 10H <sub>2</sub> O (Equivalent)	. . . . .	$P = 161$ grams
" " (Density) . . . . .	. . . . .	$D = 1.463$
" " (Volume) . . . . .	. . . . .	$V = \frac{P}{D} = 110.0$ c. c.

The volume of the anhydrous salt, 26.5 c. c. added to the volume of 10H<sub>2</sub>O = 90, gives 116.5 c. c., whereas the actual volume of the crystallised salt is only 110 c. c. Consequently:

1. Sodium sulphate and water, in uniting to form the crystallised hydrate, suffer a contraction of 6.5 for 116.5, i.e.  $\frac{1}{18}$ th of the total volume.

2. When 1 eq. (71 grams) of anhydrous sodium sulphate is dissolved in a litre of water, a liquid is obtained whose density = 1.0606, and volume therefore = 1099.8 c. c.; and as the volume of the anhydrous salt itself is 26.5, the total volume of the two has suffered by solution a contraction of 20.5 - 9.8 = 16.7 c. c.

3. When 1 eq. (161 grams) of crystallised sodium sulphate is dissolved in a litre of water, the density of the solution is 1.0559 and its volume 1099.5 c. c.; and as the crystallised salt itself has a volume = 110 c. c. the total volume has suffered a contraction of 1110.0 - 1099.5 = 10.5 c. c.

To determine the force required to compress the water, as strongly as it is contracted

by the act of dissolving the salt, the above-mentioned numbers, 7576 heat-units and 21.34 atmospheres, must be multiplied by the number of cubic centimeters in each case. The results are given in the following table :

TABLE V.

1 eq. salt dissolved in 1 litre of water	Contraction of volume	Contraction measured in Heat-units	Contraction measured in Atmospheres	Heat-units observed in the Calorimeter
Anhydrous salt . . .	16.7 c. c.	126519	356	+ 354
Hydrate . . . . .	10.5	79518	224	- 9300
Crystallisation . . .	6.5	49244	139	+ 9654

The calculated numbers in the third column differ greatly from those in the last, which are obtained by direct observation. Now the water, in dissolving the salt, gives up to it almost all the heat developed by its own contraction. If then  $T$  and  $T'$  denote the numbers of heat-units equivalent to the internal work expended in the combination of the anhydrous and hydrated salts respectively with water, we have for the anhydrous salt,  $T + 354 = 126519$  heat-units, therefore  $T = 126165$ ; and for the hydrate,  $T' - 9300 = 79518$  units, therefore  $T' = 88818$ . Hence  $T - T' = 37317$  heat-units, which number expresses the quantity of heat given up by the water ( $10\text{H}_2\text{O}$ ) to the salt  $\text{SO}^*\text{Na}$  to form the crystallised salt  $\text{SO}^*\text{Na} + 10\text{H}_2\text{O}$ , and agrees approximately with the experimental number 39590 given at the end of the following table.

The value and distribution of the work are therefore as follows:—

TABLE VI.

		Heat-units
Units of heat evolved by the water for contraction of . . .	$\left\{ \begin{array}{l} 16.7 \text{ c.c. in } \text{SO}^*\text{Na} + \text{Aq} \\ 10.5 \text{ c.c. in } \text{SO}^*\text{Na}.10\text{H}_2\text{O} + \text{Aq} \\ 6.5 \text{ c.c. in } \text{SO}^*\text{Na} + 10\text{H}_2\text{O} \end{array} \right.$	$\left\{ \begin{array}{l} 126,519 \\ 79,548 \\ 49,244 \end{array} \right.$
Algebraic sum of the Heat-units given by the Calorimeter . . .	$\left\{ \begin{array}{l} \text{SO}^*\text{Na} + \text{Aq} \\ \text{SO}^*\text{Na}.10\text{H}_2\text{O} + \text{Aq} \\ \text{SO}^*\text{Na} + 10\text{H}_2\text{O} \end{array} \right.$	$\left\{ \begin{array}{l} + 354 \\ - 9,300 \\ + 9,654 \end{array} \right.$
Heat-units as measure of the in- ternal work of combination between salt and water . . .	$\left\{ \begin{array}{l} \text{SO}^*\text{Na} + \text{Aq} \\ \text{SO}^*\text{Na}.10\text{H}_2\text{O} + \text{Aq} \\ \text{SO}^*\text{Na} + 10\text{H}_2\text{O} \end{array} \right.$	$\left\{ \begin{array}{l} 126,165 \\ 88,848 \\ 39,590 \end{array} \right.$

*The Alums.*—The salts of this group are particularly well adapted for the enquiries under consideration, on account of their great resemblance to one another in form and composition.

The following tables exhibit the quantities of heat developed or absorbed in the solution of these salts in water under various conditions:—

TABLE VII.

*Thermic action in the solution of 1 eq. of an alum in a large quantity (about 1000 eq.) of water.*

Alums	Equivalents	Heat-units at 8°-11°	Heat-units at 19°-20°
Potassium alum . . . . .	474.5	- 9803	- 9883
Ammonium alum . . . . .	453.5	- 9580	- 9631
Potassio-chromic alum . . . . .	500.5	- 9651	- 9490
Ammonio-chromic alum . . . . .	479.5	- 9628	- 9889
Potassio-ferric alum . . . . .	503.0	- 16016	-
Ammonio-ferric alum . . . . .	482.0	- 16571	- 18060

These numbers show that the action of water on the first four alums at the temperatures of experiment is nearly the same. The last two, on the other hand, undergo a greater amount of separation. The experiments with ammonio-ferric alum show that at the higher temperature (19°-21°) a still greater separation of the constituent salts takes place.

The quantities of heat absorbed were found not to vary sensibly when the salts were dissolved in comparatively small quantities of water, so small indeed as to become saturated with them.

The following table shows the quantities of heat evolved when the alums dried at  $85^{\circ}$  were dissolved in water at  $20^{\circ}$ . Most of them when dried at  $85^{\circ}$  retain 10 mols. of water, but the ammonio-ferric salt melts below  $85^{\circ}$  and loses 42.72 p. c., or 23 mols. water, and afterwards dissolves so slowly and imperfectly as to be unfit for thermic determinations. To obtain the total heat of hydration of the alums which still retain 10 mols. water, the numbers in the fourth column must be increased by those which represent the thermic effect produced on dissolving the 24-hydrated salts in water, that is to say the numbers in Table VII. but with opposite sign.

TABLE VIII.

Alums dried at $85^{\circ}$	Molecules of water still present	Equivalents		Heat of Hydration
Potassio-aluminic alum . .	10.00	348.50	12.416	22.047
Ammonio-aluminic alum . .	10.83	335.00	12.093	21.724
Potassio-chromic alum . .	11.67	389.50	3.825	
Ammonio-chromic alum . .	10.75	360.25	4.851	

The evolution of heat—more than 12,000 units—which accompanies the solution of the 10-hydrated aluminic alums may be regarded as the difference between the total heat which would be evolved in the conversion of the 10-hydrated into the 24-hydrated salts, and the quantity absorbed in the solution of the latter in water.

There is, however, another way in which the phenomenon may be viewed. The contraction which generally takes place in the solution of salts is accompanied by a considerable evolution of heat, arising from the great resistance which water offers to compression; in fact, those salts which evolve most heat in dissolving, likewise give rise to the greatest amount of contraction; and the calorific effect actually observed is the difference between the absorption of heat resulting from the disintegrating action of the water which brings about the destruction of the crystalline edifice, and the disengagement of heat proceeding from the contraction of the total volume which takes place when the salt is dissolved. Moreover, the 24 mols. of water which exist in the alums in the solid state, would, if uncombined, require 17,000 heat-units to pass into liquid state; but the chromium and aluminium alums in dissolving absorb only about 9,500 units. It would seem, therefore, that the latent heat of water is considerably diminished when it is associated with the saline constituents of crystallised alums.

The behaviour of the violet chrome-alums is peculiar. When a solution of one of these salts is kept boiling for a considerable time, it becomes green and uncrystallisable, and the solution of the salt thus modified gives, when treated with barium chloride in the cold, only a slight precipitate; the filtered liquid also gradually becomes turbid, showing that the precipitation is taking place gradually; at length, however, all the sulphuric acid is thrown down. If to a solution of violet chrome-alum modified as above, the quantity of barium chloride required to throw down all the sulphuric acid be added in four equal portions, the first two portions will be precipitated directly and completely, whereas the third and fourth portions will give rise to a slow precipitation. Hence Favre et Valson infer that the formula of green chromic sulphate is  $\text{SO}_4[\text{Cr}(\text{SO}_4)_2]$ , the group  $\text{Cr}(\text{SO}_4)_2$  being regarded as a metallic radicle, *sulphochromyl*.

These results are corroborated by the thermic phenomena exhibited in the successive precipitations of the sulphuric acid by barium chloride. Table IX. gives the quantities of heat evolved in the precipitation of modified solutions of the chrome-alums by barium chloride in halves and in fourths:—

TABLE IX.

Chrome-alums	Excess of Barium Chloride (A.)	1. half	2. half	1. fourth	2. fourth	3. fourth
Potassio-chromic alum . .	8251 heat-units	8142 h.u.	204 h.u.	4104 h.u.	4102 h.u.	146 h.u.
Ammonio-chromic alum . .	7641 "					



Here it is seen that the first two of the four precipitations give rise to equal developments of heat, whereas the calorific effect of the third is much smaller. The difference between the quantities of heat evolved in the precipitation of the two chromo-alums by excess of barium chloride (column A), seems to show that these two salts are not modified by water in exactly the same manner.

The numbers in the last three columns show that the precipitable sulphuric acid proceeds from both the sulphates contained in the double salt. But since, as the following numbers show, the decomposition of potassium sulphate by barium chloride gives about 3,800 heat-units, the precipitation of the sulphuric acid of sulpho-chromyl sulphate, if this salt were alone present, would give about 4,900 units, that is to say, as much as the decomposition of barium chloride by free sulphuric acid:

TABLE X.

Potassium sulphate precipitated by barium chloride gives	.	.	.	Heat-units
Ammonium sulphate	"	"	"	3,357
Free sulphuric acid	"	"	"	3,279
	"	"	"	5,053

An equivalent of aluminium sulphate precipitated by 3 eq. of barium chloride develops 11,877 units of heat, and if the 3 eq. be added separately, the successive quantities of heat evolved are nearly equal to one-third of this amount.

The following table gives the quantities of heat evolved on precipitating the several alums and their constituent salts with barium chloride, both directly after preparation, and after standing for a considerable time:—

TABLE XI.

Alums	Precipitation immediately after preparation	Precipitation after 14 days	Immediate precipitation of the Constituent Salts	Precipitation of Constituent Salts after 14 days
Potassio-aluminic alum . .	15,026	14,944	14,893	14,902
Ammonio-aluminic alum . .	14,888	14,650	14,812	14,787
Potassio-chromic alum . .	14,767	13,623		
Ammonio-chromic alum . .	14,636	13,900		
Potassio-ferric alum . .	18,161	18,092		
Ammonio-ferric alum . .	18,288	18,399		

These numbers show: (1.) That no alteration is produced by keeping, in the solutions, of any of the alums, excepting the chrome-alums, which appear to be modified by keeping in the same manner as by boiling. (2.) That the heat evolved in the precipitation of the two aluminic alums is nearly the same as that which is developed by the precipitation of their constituent salts. Hence it follows that these alums can neither be produced from their constituent salts within an aqueous solution, nor can they subsist in aqueous solution after they have been formed by crystallisation.

If from the nearly 15,000 heat-units evolved in the precipitation of the first four alums by barium chloride, we deduct the 3,300 units developed by the precipitation of potassium or ammonium sulphate, there remain 11,700 units due to the precipitation of the aluminium sulphate contained in the alums. This number agrees nearly with that found by direct observation. Divided by 3, it gives 3,900 for the quantity of heat due to the precipitation of 1 mol. sulphuric acid from the aluminium sulphate. But the precipitation of barium chloride by free sulphuric acid gives about 5,000 heat-units, that is to say considerably more. With the iron-alums it is otherwise: for on subtracting from the 18,300 heat-units of the last table likewise the number 3,900, there remain 15,000 units, the third of which, viz. 5,000, is the same as the amount of heat developed in precipitation by free sulphuric acid. This seems to show that in the iron-alums the disuniting action of the water goes further than with the other alums, not only separating the constituent sulphates one from the other, but likewise resolving the ferric sulphate itself into acid and base.

The following table gives the quantities of heat developed in the successive precipitation of the sulphuric acid of various alums;—

TABLE XII.

Alums	1. half	2. half	1. fourth	2. fourth	3. fourth	4. fourth
Potassio-aluminic .	7,601	7,815				
Potassio-chromic .	7,514	7,388	3,680	3,702	3,665	3,699
Ammonio-ferric .			4,570	4,600	4,793	4,712

When a sufficiently dilute solution of a ferric alum is heated, its original brown colour becomes gradually lighter, and at length like that of cobalt solutions; if the liquid be then heated for some time to the boiling point, a more or less considerable quantity of ferric oxide is precipitated, containing small quantities of sulphuric acid. This is shown by the following numbers:—

TABLE XIII.

	Ammonio-ferric alum			Potassio-ferric alum
	1.	2.	3.	
Fe <sup>2</sup> O <sup>3</sup> { precipitated .	64.3	66.3	59.1	76.1
{ not precipitated .	16.1	13.2	21.0	4.7
SO <sup>2</sup> { precipitated .	5.4	5.8	41.1	60.3
{ not precipitated .	186.0	185.6	151.5	130.9

The effect appears to be due to the disuniting action of the heat superadded to that of the water, a view confirmed by the thermic results obtained on precipitating the ferric alums by ammonia (*Compt. rend.* lxxiv. 1016, 1065; *Chem. Centr.* 1872, 457, 475).

Favre & Valson have also studied the solution of the alums in water with reference to the alterations of physical state, more especially the contraction in volume—the *coercive effect*, as they designate it—thereby produced (*Compt. rend.* lxxv. 798, 925, 1000, 1066; *Chem. Centr.* 1872, 572, 730; 1873, 42).

The results were obtained by two methods: first, by a comparison of the densities of the solid salts and the solutions; secondly, by observing the increase of volume caused by the solution of a known weight of the salt in a determinate quantity of water contained in a reservoir surmounted by a narrow calibrated tube. Table XIV. contains the direct results of observations; Table XV. the results deduced therefrom. To render these numbers comparable, the formulae of the salts examined are all reduced to 1 eq. of sulphuric acid. Column *P* contains the equivalent (molecular) weights of the salts. The numbers in columns *d*, *h*, *dh*, refer to *normal solutions*, that is to say, solutions containing 1 eq. of the salt in a litre of water. Column *d* shows the densities of the salts; column *h* the heights in millimeters to which the respective solutions rise in capillary tubes of  $\frac{1}{4}$  mm. diameter. These and the following observations were made at a temperature of 20°. Column *dh* gives the products of the densities and capillary heights. The numbers in column *v* express the increase of volume which the water acquires by solutions of 1 eq. of the salt. These values are easily calculated from the densities of the solutions. For, supposing that a weight *x* of the salt is dissolved in a litre of water, so that the total weight of the solution is 1 + *x*, further that 1 + *y* is the density of the solution, and 1 + *v* the volume, we have 1 + *v* =  $\frac{1+x}{1+y}$ , therefore  $v = \frac{x-y}{1+y}$ .

Column *D* contains the densities of the salts in the anhydrous state; column *V* their volume =  $\frac{P}{D}$ . Before solution, the total volume is 1 + *V*, after solution it is

1 + *v*; consequently, *V* - *v* is the contraction, and the quotient  $\frac{V-v}{V}$  is the coefficient of contraction, that is to say, the contraction of the solution referred to the unit of volume. These numbers are given in the last two columns of the second table.

TABLE XIV.

Names of the salts		Temperature	Density
		°	
Potassium sulphate . . . .		21.8	2.653
Ammonium sulphate . . . .		22.3	1.786
Aluminium sulphate, dehydrated		22.5	2.672
Aluminium sulphate, crystallised		22.1	1.767
With 24H <sub>2</sub> O	Potassio-aluminic alum . . . .	21.9	1.745
	Ammonio-aluminic alum . . . .	21.5	1.634
	Potassio-ferrie alum . . . .		
	Ammonio-ferrie alum . . . .	22.1	1.712
	Potassio-chromic alum . . . .	21.5	1.816
	Ammonio-chromic alum . . . .	21.9	1.697
Dehydrated	Potassio-aluminic alum . . . .	22.0	2.617
	Ammonio-aluminic alum . . . .	20.0	2.333
	Potassio-ferrie alum . . . .		
	Ammonio-ferrie alum . . . .	22.0	2.492
	Potassio-chromic alum . . . .	20.9	2.713
	Ammonio-chromic alum . . . .	21.0	2.472
<i>Normal solutions</i>			
Potassium sulphate . . . .		21.8	1.0662
Ammonium sulphate . . . .		22.3	1.0378
Aluminium sulphate . . . .		22.0	1.0568
Potassio-aluminic alum . . . .		21.8	1.0595
Ammonio-aluminic alum . . . .		21.8	1.0521
Potassio-ferrie alum . . . .		15.6	1.0600
Ammonio-ferrie alum . . . .		21.8	1.0535
Potassio-chromic alum, violet		21.0	1.0636
Ammonio-chromic alum, violet		21.0	1.0567
Potassio-chromic alum, green		22.0	1.0602
Ammonio-chromic alum, green		22.0	1.0517

The density of an anhydrous potassio-aluminic alum shows that it is a chemical compound, not a mere mixture of its constituents: for the sum of the weights of the constituent salts divided by the sum of their volumes gives the number 2.665, whereas the actual density of the alum is only 2.617. With ammonio-aluminic alum, on the contrary, the observed density, 2.333, is very nearly the same as the mean density of the constituent salts, namely, 2.337. Nevertheless it is most probable that this salt is also a chemical compound, inasmuch as it does not give off ammonium sulphate till raised to a temperature much higher than that at which ammonium sulphate volatilises when heated by itself. The same is the case with the other ammonia alums.

The relations of volume and density of the crystallised alums are given in Table XVI.

As the values of  $V$  differ but slightly, it may be assumed that the molecular volumes of all the crystallised alums are equal.

The values  $V_1 - v_1$  measure the contraction which the water undergoes by dissolving the hydrated salts. If from these we subtract the corresponding values  $V - v$  in Table XV, which measure the contraction consequent on the solution of the anhydrous salts, the differences will give the portion of the contraction which is a consequence of the formation of crystals. For potassio-aluminic alum, for example,  $V - v = 19.86$  and  $V_1 - v_1 = 9.17$ ; and the difference of these numbers, 10.69, is greater than  $V - v$  itself, showing that the contraction produced by the crystallisation is greater than that which is a consequence of the solution of the hydrated salt. Direct experiments with sodium sulphate have shown that for this salt the reverse takes place (p. 294).

The conversion of the violet solutions of the chrome-alums into green is accompanied by a diminution of the density of the liquid. Normal solutions of the two violet chrome-alums were heated in sealed tubes to the boiling temperature, and their densities

TABLE XV.

Anhydrous salts	Formula	Equivalent weight $\frac{P}{P}$	Normal solutions $\left\{ \begin{array}{l} d \\ h \\ dh \end{array} \right.$			D	Equivalent volume $\frac{P}{V} = \frac{P}{D}$	v	V - v	$\frac{V-v}{V}$
Potassium sulphate . . .	SO <sup>4</sup> K . . .	87.00	1.0662	58.2	61.9	2.653	32.80	19.71	13.09	0.396
Ammonium sulphate . . .	SO <sup>4</sup> Am . . .	66.00	1.0378	59.7	61.9	1.766	37.38	26.98	10.40	0.275
Aluminium sesquisulphate . . .	SO <sup>4</sup> Al $\frac{3}{2}$ . . .	57.17	1.0568	58.1	61.4	2.672	21.38	0.35	21.28	0.996
Potassio-aluminic alum . . .	SO <sup>4</sup> $\left( \frac{3Al\frac{3}{2}K}{4} \right)$	64.62	1.0505	58.0	61.4	2.617	24.60	4.83	10.86	0.805
Ammonio-aluminic alum . . .	SO <sup>4</sup> $\left( \frac{3Al\frac{3}{2}Am}{4} \right)$	59.33	1.0521	58.4	61.4	2.333	25.43	6.00	18.55	0.730
Potassio-ferric alum . . .	SO <sup>4</sup> $\left( \frac{3Fe\frac{3}{2}K}{4} \right)$	71.78	1.0600	57.8	61.3	"	"	11.11	"	"
Ammonio-ferric alum . . .	SO <sup>4</sup> $\left( \frac{3Fe\frac{3}{2}Am}{4} \right)$	66.50	1.0535	58.3	61.4	2.492	26.69	12.34	14.35	0.537
Potassio-chromic alum . . .	SO <sup>4</sup> $\left( \frac{3Cr\frac{3}{2}K}{4} \right)$	71.12	1.0636	57.9	61.5	2.713	26.21	7.07	19.14	0.730
Ammonio-chromic alum . . .	SO <sup>4</sup> $\left( \frac{3Cr\frac{3}{2}Am}{4} \right)$	65.87	1.0567	58.2	61.3	2.472	26.65	8.68	17.97	0.675

TABLE XVI.

Formula	P	D	$V' = \frac{P}{D}$		$r_1$	$V_1 - r_1$	$\frac{V_1 - r_1}{V_1}$
$\text{SO}^4 \left( \frac{3\text{Al}\frac{3}{2}\text{K}}{4} \right) + 6\text{HO}$	118.62	1.745	67.98	1.0565	58.81	9.17	0.135
$\text{SO}^4 \left( \frac{3\text{Al}\frac{3}{2}\text{Am}}{4} \right) + 6\text{HO}$	113.33	1.634	69.36	1.0497	60.62	8.74	0.126
$\text{SO}^4 \left( \frac{3\text{Fe}\frac{3}{2}\text{K}}{4} \right) + 6\text{HO}$	125.78	1.827	68.84	1.0560	65.18	3.66	0.053
$\text{SO}^4 \left( \frac{3\text{Fe}\frac{3}{2}\text{Am}}{4} \right) + 6\text{HO}$	120.50	1.712	70.38	1.0508	66.35	4.03	0.057
$\text{SO}^4 \left( \frac{3\text{Cr}\frac{3}{2}\text{K}}{4} \right) + 6\text{HO}$	125.12	1.816	68.90	1.0604	61.04	7.86	0.114
$\text{SO}^4 \left( \frac{3\text{Cr}\frac{3}{2}\text{Am}}{4} \right) + 6\text{HO}$	119.87	1.697	70.64	1.0538	62.70	7.94	0.112
$\text{SO}^4\text{Al}\frac{3}{2} + 6\text{HO}$	111.17	1.767	62.90	1.0539	51.34	8.56	0.136

afterwards determined at 22°. These densities were found to be 1.0572 and 1.0402, numbers differing from those in Table XVI. viz., 1.0636 and 1.0567, which were determined before the solutions had been heated. The diminution of density in the solutions of the two chrome-alums is nearly the same.

The numbers in Table XV. under the head of normal solutions, afford the means of extending to the alums the relations of density and capillary height formerly established by Valson for other salts (pp. 244-246). The following are the moduli of density and capillarity of the several metals contained in the alums, deduced from the numbers in Table XV. a solution of ammonium sulphate being taken as the standard:—

TABLE XVII.

	Moduli of density	Moduli of capillarity
Ammonium (Am) . . . . .	0.0000	0.0
Potassium (K) . . . . .	0.0284	1.5
Aluminium (Al $\frac{3}{2}$ ) . . . . .	0.0190	1.7
Iron (Fe $\frac{3}{2}$ ) . . . . .	0.0209	1.9
Chromium (Cr $\frac{3}{2}$ ) . . . . .	0.0252	2.0

The moduli of density are the numbers which must be added to the density of a normal solution of ammonium sulphate 1.0378 to obtain the densities of the other normal solutions. The moduli of capillarity are the numbers which must be subtracted from the capillary height of ammonium sulphate, 59.7, in a tube 5 millimeters in diameter, to obtain the capillary heights of the other normal saline solutions (p. 246). The following table exhibits the agreement between the observed and calculated results:—

TABLE XVIII.

Normal solutions of alums	Density		Capillary calc.	Height obs.
	Calc.	Obs.		
Potassio-aluminic alum . . . . .	1.0591	1.0595	58.0	58.0
Ammonio-aluminic alum . . . . .	1.0520	1.0521	58.4	58.4
Potassio-ferric alum . . . . .	1.0606	1.0600	57.9	57.8
Ammonio-ferric alum . . . . .	1.0535	1.0535	58.3	58.3
Potassio-chromic alum . . . . .	1.0638	1.0636	57.8	57.9
Ammonio-chromic alum . . . . .	1.0567	1.0567	58.2	58.2

The product of the height of each normal solution into its density gives the numbers in column  $dh$  of Table XV. which are nearly the same for all the alums.

These results confirm the conclusion deduced from the thermic phenomena before considered, namely, that double salts, and especially the alums, cannot exist in presence of water, but are resolved into their constituent salts; both for the density and for the capillary height the same numbers are obtained, whether by direct determination with solutions of the alums, or by calculations from the numbers belonging to the constituent salts (*Compt. rend.* lxxv. 798 and 925; *Chem. Centr.* 1872, 572, 730).

A comparison of the thermic effects and the alterations of volume accompanying the solution of the alums leads to the following conclusions:—

The numbers in column  $v$  of Table XV. show that different salts in dissolving undergo very different changes of volume; for whereas ammonium sulphate increases by about 27 c. c. for 1 eq., potassium sulphate increases by only 20 c. c., and aluminium sulphate by only 0.35 c. c. The solution of the sulphates of potassium and ammonium is attended with a fall of temperature, whereas aluminium sulphate exhibits a considerable rise. The slowness with which this salt dissolves when in the anhydrous state renders it unfit for calorimetric experiments, but when dehydrated at  $200^{\circ}$  and then brought back to the composition  $Al_2(SO_4)_3 \cdot 6H_2O$  it gives 23919 heat-units in dissolving. If it could be employed in the anhydrous state, it would doubtless give a higher number.

These examples, together with those formerly cited, show that there is a certain connection between the thermic phenomena and the contraction of volume attending the solution of salts. The hydrated alums, in dissolving, exhibit a contraction smaller than that which might be expected from a comparison of the values obtained for  $v_1$  and  $V_1$ ; but at the same time the act of solution is accompanied by an absorption of heat, amounting to about 10,000 units in the case of chrome-alum with 24 eq. water, and to 18,000 units in that of the ferric alums with the same amount of water. Nearly the same absorption of heat is likewise observed in the solution of the aluminic alums; at the same time the values of  $v_1$  and  $V_1$  show that the corresponding contractions are nearly the same; the latter observation applies also to the iron-alums. On the other hand, the contractions which take place in the solution of the anhydrous alums are greater than those which accompany the solution of the hydrated alums.

The partially dehydrated alums exhibit in dissolving, not an absorption but a development of heat; thus potassio-aluminic alum with 10H<sub>2</sub>O gives + 12,416 heat-units instead of - 9,803 (the absorption observed with the 24-hydrated salt), making altogether a difference of 22,219 heat-units. This difference would be much greater if it were possible to operate with perfectly anhydrous alums.

In examining the relations between the phenomenon of contraction and the external thermic effects accompanying the solution of salts, it must be borne in mind that solution is a complex effect resulting from several different forms of work, of which only the final result can be directly observed.

This has already been explained in the case of sodium sulphate. Table XIX. will facilitate the application of similar considerations to the alums.

In this table  $V_1$ ,  $v_1$ ,  $V$  and  $v$ , have the same values as before. The column  $V_2 = V + 6H_2O$  contains the volumes of the anhydrous salts plus that of their water of crystallisation in the uncombined state; hence, as  $V_1$  is the volume of the crystallised salt, the differences  $V_2 - V_1$  measure the contractions which take place on assumption of the water of crystallisation. Lastly, the differences  $V - v$  denote the contractions which accompany the solution of the hydrated salt, and  $V_1 - v$ , those which ensue on the solution of the crystallised salt. The sum of the values  $V_2 - V_1$  and  $V_1 - v$  is necessarily  $V_2 - v$ : for the ultimate state of a solution must be the same whether it is made from the hydrated or from the anhydrous salt, and consequently the contraction produced by the anhydrous salt must be equal to that produced by the hydrated salt together with that resulting from the addition of the action of crystallisation.

When the values of  $v$  are calculated for the first two alums, starting from the corresponding values for aluminium sesquisulphate and for the sulphates of potassium and ammonium, we obtain the numbers 5.19 and 7.00, agreeing approximately with 4.83 and 6.88. A similar calculation for the same alums with respect to the values  $V - v$  gives the numbers 19.4 and 18.37, agreeing approximately with 19.86 and 18.65. For the other alums, however, this calculation cannot be carried out, because the densities of the anhydrous ferric and chromic sulphates are unknown. Nevertheless, the above-mentioned coincidences seem to show that moduli of contraction exist analogous to those previously established for the thermal phenomena densities and capillary actions.

Table XX. exhibits the quantities of heat, which, according to principles previously developed, correspond with the work of the solution.  $V - v$  denotes the

TABLE XIX.

Formulae of the Salts	V	V <sub>1</sub>	V <sub>2</sub> = V + 6HO	V <sub>2</sub> - V <sub>1</sub>	v	V - v	v <sub>1</sub>	V <sub>1</sub> - v <sub>1</sub>
SO <sup>+</sup> K . . . . .	32.80	"	"	"	10.71	13.09	"	"
SO <sup>+</sup> Am . . . . .	37.88	"	"	"	26.98	10.40	"	"
SO <sup>+</sup> Al <sub>3</sub> . . . . .	21.38	"	"	"	0.35	21.03	"	"
SO <sup>+</sup> ( $\frac{3Al_3K}{4}$ ) + 6HO . . . . .	24.69	67.98	78.69	10.71	4.83	19.86	58.81	9.17
SO <sup>+</sup> ( $\frac{3Al_3Am}{4}$ ) + 6HO . . . . .	25.43	69.36	79.43	10.07	6.88	18.55	60.62	8.74
SO <sup>+</sup> ( $\frac{3Fe_3K}{4}$ ) + 6HO . . . . .	26.45	68.84	80.45	11.61	10.54	15.91	65.18	3.66
SO <sup>+</sup> ( $\frac{3Fe_3Am}{4}$ ) + 6HO . . . . .	26.69	70.38	80.69	10.31	12.34	14.35	66.35	4.03
SO <sup>+</sup> ( $\frac{3Cr_3K}{4}$ ) + 6HO . . . . .	26.21	68.90	80.21	11.31	7.07	19.14	61.04	7.86
SO <sup>+</sup> ( $\frac{3Cr_3Am}{4}$ ) + 6HO . . . . .	26.65	70.64	80.65	10.01	8.68	17.97	63.70	7.94
SO <sup>+</sup> Al <sub>3</sub> + 6HO . . . . .	21.38	62.90	75.38	12.46	0.35	21.03	54.34	8.56

internal work which measures the contractive force exerted by the salt in the water.  $V_2 - V_1$  measures the work employed in the formation of the crystal, and  $V_1 - v_1$  the work which is rendered available on the solution of the crystallised salt. The numbers in this table were obtained by multiplying the corresponding numbers of the preceding table by 75.76, which number answers to the quantity of heat abstracted from a litre of water when its volume is diminished by 1 c. c.

TABLE XX.

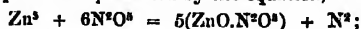
Formulae of the Salts		$V - v$	$V_1 - v_1$	$V_2 - V_1$
		Heat-units	Heat-units	Heat-units
SO <sup>4</sup> K	. . . . .	99,170	—	—
SO <sup>4</sup> Am	. . . . .	78,700	—	—
SO <sup>4</sup> Al $\frac{1}{2}$	. . . . .	159,323	64,851	94,851
Alums	Potassio-aluminic . . . . .	150,450	69,472	81,139
	Ammonio-aluminic . . . . .	140,535	66,214	76,290
	Potassio-ferric . . . . .	120,534	27,728	93,109
	Ammonio-ferric . . . . .	108,716	30,531	78,109
	Potassio-chromic . . . . .	145,005	59,547	85,685
	Ammonio-chromic . . . . .	136,141	60,153	75,836

The interpretation of these numbers leads to the same or similar consequences as those which have already been developed in the case of sodium sulphate (p. 294).

The numbers in the last table are very high, and out of all proportion to those obtained with the calorimeter, which are for the most part very low and not unfrequently negative. They cannot be explained either by the fusion of the crystallisation-water or by that of the salts themselves. The mechanical work corresponding with these large quantities of heat seems indeed to indicate considerable modifications of internal structure. The solvent action of the water may perhaps consist in separating the elements of the salt and bringing them, if not into the free state, at least into a state of partial independence, very different from that in which they existed in the original salt. The existence of such a state is, moreover, indicated, as already explained, by the phenomena of density, capillarity, and contraction. Starting from these different points of view, we always arrive at the same conclusion, namely that in sufficiently dilute saline solutions, each of the metallic and chlorous radicles produces effects which are independent of those produced by all the rest.

Finally, Favre and Valson sum up their results in the following theorem: 'Solution brings the elements of the dissolved bodies into a state of mutual independence, and the internal mechanical work required for the production of this effect is measured by the alterations of volume which take place in the act of solution, and consequently by that quantity of heat which comes into play as soon as the same effects of contraction (coercion) are produced in the solvent by equivalent quantities of work' (*Compt. rend.* lxxv. 1000).

**Nascent State.** According to H. Sainte-Claire Deville (*Compt. rend.* lxx. 20, 550) the assumption of a so-called nascent state in bodies ascribes to them a system of arbitrarily chosen properties, which contributes nothing to the explanation of chemical reactions. By the examination of a number of phenomena in which this peculiar state of bodies is supposed to come into play, such as the action of zinc on solutions of nitric acid, of sulphuric and nitric acid, and of hydrochloric and nitric acid, the ultimate result of which is the formation of sulphate, nitrate or chloride of zinc and of ammonia, Deville found that hydrogen is never evolved in contact with the zinc at any temperature or any degree of concentration of the nitric acid, and that the quantity of ammonia formed is altogether independent of the concentration of the acid. When zinc is treated with excess of nitric acid, the resulting solution contains nitrous acid, a little nitrogen dioxide, often a large quantity of nitrogen monoxide, very little nitrogen, and finally ammonia. These results are explained by Deville as follows:—The evolution of nitrogen takes place as represented by the equation,

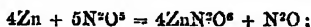


and, assuming that the acid was contained in the liquid in the form of the hydrate  $\text{N}^{\text{a}}\text{O}^{\text{a}}.2\text{H}^{\text{a}}\text{O}$ , and that it loses 5 at oxygen, there will remain ammonium nitrate  $\text{NH}^{\text{a}}.\text{NO}^{\text{a}} = \frac{1}{2}(\text{N}^{\text{a}}\text{H}^{\text{a}}\text{O.N}^{\text{a}}\text{O}^{\text{a}})$ . Moreover, experiment shows that only a portion of the liberated nitrogen remains united with the elements of water, the rest emerging



as gas. This, according to Deville, explains the formation of nitrous acid, nitrogen, and part of the ammonia.

The evolution of nitrogen monoxide takes place according to the equation,



and assuming, as before, that the hydrate  $\text{N}^2\text{O}^3 \cdot 2\text{H}^2\text{O}$ , or  $2\text{NO}^2\text{H} \cdot \text{H}^2\text{O}$ , is present in the liquid and gives up 4 at. oxygen to the zinc, there will remain ammonium nitrate  $\text{NH}^4\text{NO}^3 = \frac{1}{2}(\text{N}^2\text{H}^4\text{O} \cdot \text{N}^2\text{O}^3)$ . Only a part of the nitrogen monoxide, however, remains combined with the elements of water, the rest escaping as gas or remaining dissolved.

Dewille has also found—by a large number of experiments in which the proportional quantities of ammonia, nitrogen monoxide, nitrogen and nitrous acid, formed in a liquid of known temperature, concentration, and tension of the dissolved gases, were determined—that the quantity of ammonia formed and the quantity of zinc required to produce it from nitric acid, do not vary much with the concentration of the acid. As the concentration becomes greater, the quantity of nitrogen evolved decreases and that of nitrogen monoxide increases.

When zinc acts upon a mixture of sulphuric and nitric acids, the quantity of hydrogen evolved diminishes as the proportion of nitric acid increases, and after a certain time, no more hydrogen is evolved. Hence it is inferred that the two acids act upon the zinc just as if each of them were present alone. When the nitric acid is in excess, the bars of zinc become surrounded with a layer of saline solution containing a large proportion of zinc nitrate. Around this layer the sulphuric acid rapidly decomposes the zinc nitrate, reproducing free nitric acid, which again dissolves zinc; and thus the action goes on, the sulphuric acid never coming into direct contact with the zinc. This accounts for the complete disappearance of the hydrogen.

A mixture of hydrochloric and nitric acids likewise acts upon zinc as if the acids were separate, and not as if they had previously formed aqua regia, which would decompose the ammonia. Moreover, sulphuric acid dissolves zinc less quickly than hydrochloric acid, and in such proportion that 0.29 eq. of nitric acid is sufficient to arrest completely the action of 1 eq. sulphuric acid, whereas to stop the action of 1 eq. hydrochloric acid, 0.67 eq. nitric acid is required. Lastly, sulphuric acid very easily displaces the nitric acid of zinc nitrate, whereas the conversion of this salt into chloride, requires a very large excess of hydrochloric acid and prolonged boiling. Hence, when a layer of dissolved zinc nitrate has formed around the zinc, hydrochloric acid can more easily penetrate this layer without decomposing the zinc nitrate, and thus reach the zinc and give off hydrogen.

All these reactions may, therefore, be referred to simple mechanical effects analogous to the polarisation of the electrodes or the elements of a battery, in which the chemical action is arrested by a layer of gas which prevents the liquid from coming in contact with the metals.

**Influence of certain Liquids in retarding or arresting the action of Acids on Metals.**—(Marangoni a. Stefanelli, *Il nuovo Cimento*, [2] iv. 373). The evolution of hydrogen from dilute sulphuric acid by the action of zinc is quickly arrested on adding a small quantity of an essential oil, such as oil of myrtle, thyme, lavender, turpentine, or cherry-laurel, and agitating briskly with a glass rod, but recommences, though less strongly, on addition of a certain quantity of alcohol. Fixed oils likewise arrest the action completely, but less quickly than essential oils; ether, naphtha, benzene, and nitrobenzene have but little effect, the evolution of hydrogen being merely retarded by them while the agitation continues, and recommencing soon after the liquid is left at rest. The action of dilute nitric acid on copper is retarded by essential oils while they are agitated with the liquid, but quickly recommences on repose; fixed oils produce but little retardation; ether, naphtha, benzene, and nitrobenzene scarcely any. Similar remarks apply to the effect of these various liquids on the action of hydrochloric acid upon zinc. That of dilute nitric acid on zinc is not sensibly retarded by either of them.

The retarding action in all these cases is due to the formation, on the surface of the zinc, of a film of liquid which protects the metal from contact with the acid. The agitation of the mixture facilitates the formation of this film, partly by bringing the particles of the oily liquid in contact with the metal, partly by removing the bubbles of hydrogen which adhere to its surface.

A comparison of the observations made by Marangoni a. Stefanelli with those of Duclaux (*Ann. Chem. Phys.* [4] xxi. 373) on the surface-tension of liquids, leads to the conclusion that the permanence of the protecting film is greater in proportion as the density of the oily liquid approaches more nearly to that of the acidulated water, and diminishes in proportion as this liquid has a greater superficial capillary tension (which is proportional to the product of its density into the height to which it rises in  
2nd Sup.

capillary tube of given diameter). The fixed oils produce but little retarding effect, because, though they differ but little from the acidulated water in density, they have a considerable superficial tension; ether, naphtha, and benzene, on the other hand, though their superficial tension is small, cannot form permanent films on the metal under the acidulated water, on account of their small specific gravity; but the volatile oils above mentioned have but little superficial tension, and a density (0.869—0.886) not differing greatly from that of the acidulated water: hence they have the greatest tendency to form permanent films on the surface of the zinc.

The authors also found that the effect of a film of essential oil on the zinc plates of a voltaic pile is similar to that of amalgamation, preventing local action to a certain extent. It diminishes the quantity and intensity of the current at the commencement of the action, but renders it for a certain time more constant. After two or three hours, however, it stops the action altogether.

#### CHINESE GREEN. See LOKAO.

**CHINESE OIL-BEAN.** These beans, belonging to the genus *Phaseolus*, are used in China for the production of sweet oil by pressure, while the pressed residue is made into a kind of cheese. The composition of a yellowish and a black variety, analysed by Stöckhardt (*Chem. Ackers*. 1872, 122), is given in the following table, together with that of the cake analysed by Voelcker:—

	Yellowish oil-bean	Black oil-bean	Oil-bean cake
Water . . . . .	6.60	7.14	12.82
Albuminoids . . . . .	38.51	38.04	45.93
Oil . . . . .	20.53	16.88	5.32
Non-nitrogenous extractive matter . . . . .	21.61	27.79	24.52
Crude fibre . . . . .	5.13	5.53	5.71
Ash . . . . .	4.50	4.62	5.70
	100.00	100.00	100.00

The Chinese oil-beans resemble lupine-seeds in containing no starch and a much larger proportion of fat and nitrogen than beans, peas, vetches, or lentils.

**CHINOLINE**,  $C^9H^7N$ . Lulavien's experiments with this base, shortly noticed in the *First Supplement* (p. 430), have since been published in detail (*Ann. Ch. Pharm.* clv. 311). The chinoline was prepared by Williams's process (1st *Suppl.* 869) by distilling cinchonine with potassium hydrate, and collecting apart the portion which passed over between  $215^{\circ}$  and  $245^{\circ}$ .

Potassium and sodium do not act upon chinoline at ordinary temperatures, but on applying heat, an unstable red body is formed without evolution of hydrogen, and, on removing the excess of potassium and treating the mass with water, a brown amorphous insoluble substance remains. Chinoline is not decomposed by ordinary nitric acid at the boiling heat, or by the fuming acid at ordinary temperatures, but on heating it with the latter, copious red fumes are evolved, and on addition of water, an amorphous yellow body separates out. Chinoline is not oxidised by heating with a mixture of potassium chromate and sulphuric acid, but the liquid, on cooling, deposits characteristic gold-yellow needles of acid chromate of chinoline. Melting potash produces, with chinoline, a greenish-blue, and on prolonged heating, a dark violet, unstable coloration, which disappears, with formation of a brown amorphous substance, when the fused mass deliquesces or is dissolved in water.

This colour is likewise produced when any derivative of chinoline is fused with an alkali or alkaline earth; sometimes even on fusing cinchonine with potash.

Chinoline-sulphonic acid,  $C^9H^7N.SO^2H$ , is formed when chinoline is heated with ordinary concentrated sulphuric acid, but is best prepared by heating chinoline for several days on the water-bath with fuming sulphuric acid till a drop of the solution, after dilution with water, no longer gives a turbidity with soda-ley; part of the chinoline, however, remains unattacked, even after heating for forty hours. The product is a brown opaque thickish liquid, from which the pure acid may be obtained by pouring it into a large quantity of water, saturating with baryta, precipitating the excess of baryta with the exact quantity of sulphuric acid required, and concentrating the yellow filtrate till it begins to crystallise. The acid forms large, hard, well-defined crystals, which are colourless, shining, strongly refractive, permanent in the air, and

anhydrous. It dissolves sparingly in cold, more easily in hot water or in strong hydrochloric acid; in hot alcohol more freely than in cold, but is insoluble in ether. Its solutions, like those of other chinoline derivatives, exhibit a tendency to supersaturation. The aqueous solution reddens litmus and slowly, and decomposes barium carbonate. The acid bears a rather high temperature without decomposition, but decomposes when melted on platinum-foil, giving off acid vapours and an odour of chinoline. It is not perceptibly attacked by boiling nitric acid. When fused with potash it gives off chinoline, and on treating the fused mass with water, a brown, amorphous insoluble body separates, which is dissolved by acids, and reprecipitated by alkalis. The original mass, treated with acids, gives off a small quantity of sulphur dioxide. Chinoline-sulphonic acid or its barium salt, cautiously heated with barium hydrate, gives the blue-green coloration above mentioned.

*Barium chinoline-sulphonate*,  $\text{Ba}(\text{C}^6\text{H}_5\text{SO}_3)^2$ , is prepared from the brown liquid formed by heating chinoline with fuming sulphuric acid, by pouring this liquid into a large quantity of water, supersaturating with baryta, removing the excess of barium with carbonic acid, filtering, evaporating to dryness, redissolving in boiling water, and evaporating to a small bulk. It may be heated without decomposition to  $250^\circ$ , dissolves but sparingly even in hot water, and always separates in the amorphous state on evaporation.

The *lead salt* is obtained as a white granular precipitate on mixing the aqueous solution of the acid with neutral lead acetate and ammonia, or with the basic acetate. The acid, neutralised with ammonia, does not precipitate *silver nitrate*, but the liquid, on standing, gradually deposits a white precipitate consisting of thin silky needles.

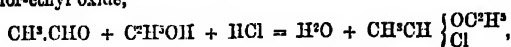
*Bromochinolines*.—When 1 mol. chinoline-sulphonic acid is heated in sealed tubes in the water-bath for about twenty-five hours with 6 atoms of bromine and a little water, the acid is resolved into sulphuric acid and bromochinolines, which separate into a solid yellow-brown substance. One part of this mass is dense and granular, the other part very loose, light, and of lighter colour. Both compounds are insoluble in water, very slightly soluble in cold, more easily in hot alcohol; they are easily separated by mechanical selection. When the denser product—which is the larger portion—was freed by water from adhering bromine, and dissolved in an insufficient quantity of hot alcohol, crystalline nodules separated containing no sulphur, a large quantity of bromine, and (after drying at  $100^\circ$ ) quantities of carbon and hydrogen indicating a composition intermediate between tri- and tetrabromochinoline. They melt at  $147^\circ$ – $150^\circ$ , are insoluble in water and in soda-ley, which latter does not attack them at the boiling heat, dissolve in strong hydrochloric acid, and are reprecipitated by water.

Liquid bromine acts at ordinary temperatures on chinoline or its aqueous solution, but the products are uncrystallisable. Better results are obtained with bromine-vapour. When a watch-glass containing 3 grams of chinoline, and a beaker containing 6 grams of bromine are placed within a bell-jar over sulphuric acid, the bromine disappears in two days, and the chinoline is converted partly into a dark red syrupy mass, partly into brown crystals. This product, probably an additive compound, forms with water a thick insoluble oil, the water turning yellow and acquiring the odour of bromine. A great part of the bromine may be removed by sulphurous acid, also with soda-ley, which does not separate chinoline from it. It is insoluble in hydrochloric acid. Alcohol dissolves it almost wholly, forming a red solution which, on standing, deposits white silky needles of tribromochinoline,  $\text{C}^6\text{H}_3\text{Br}_3\text{N}$ . This compound melts at  $173^\circ$ – $175^\circ$ , solidifies, on cooling, in radiate groups of long needles, and volatilises completely, without decomposition, at a stronger heat, emitting a faint odour somewhat like that of chinoline. It is insoluble in water, very soluble in cold, easily in hot alcohol, also in strong hydrochloric or sulphuric acid, and is precipitated by water or soda as a loose crystalline mass. It is not acted upon by aqueous or alcoholic potash, silver oxide or strong sulphuric acid. When fused with potassium hydrate, it gives the blue-green colour exhibited by all derivatives of chinoline.

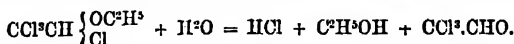
**CHLORAL**,  $\text{C}^2\text{HCl}^3\text{O} = \text{COH}^2\text{OH}^2\text{O}$ . Lieben showed in 1867 (*Compt. rend.* xlv. 1346) that the action of chlorine on alcohol at ordinary temperatures gives rise to the formation of mono-, di-, and tri-chloroacetal; and Paternò having since found that chloral can be formed by the decomposition of trichloroacetal (1st Suppl. 432), Lieben regards this series of reactions as the source of the formation of chloral by the ordinary process of passing chlorine into alcohol. The final product of the action of chlorine on *absolute* alcohol is chloral alcoholate,  $\text{C}^2\text{H}^2\text{Cl}^3\text{O}^2 = \text{CHCl}^2\text{O}^2\text{C}^2\text{H}^2\text{O}$ , (Lieben, *Deut. Chem. Ges. Ber.* iii. 907).

Another view of the formation of chloral from alcohol is given by Wurtz & Vogt (*Compt. rend.* lxxiv. 777). The action of chlorine upon alcohol first gives rise to the formation of aldehyde and hydrochloric acid;  $\text{C}^2\text{H}^2\text{O} + \text{Cl}^2 = \text{C}^2\text{H}^2\text{O} + 2\text{HCl}$

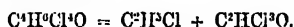
(1474); the hydrochloric acid acting upon the aldehyde and alcohol produces water and monochlor-ethyl oxide,



which latter by the further action of the chlorine is converted into tetrachlor-ethyl oxide,  $\text{CCl}_3\text{CH} \left\{ \begin{smallmatrix} \text{OC}^2\text{H}_5 \\ \text{Cl} \end{smallmatrix} \right.$ ; and this compound is converted into chloral by the action of the water either present in the alcohol or formed in the manner just mentioned:



This tetrachlorinated ether—first obtained by Malaguti by the action of chlorine on ethyl oxide (ii. 540), and likewise formed according to Henry (p. 314) by the action of phosphorus pentachloride on chloral alcoholate is in fact converted into chloral by heating with water. Heated with alcohol instead of water, it yields hydrochloric acid and trichloroacetal,  $\text{CCl}_3\text{CH}(\text{OC}^2\text{H}_5)_2$ , which may be converted into chloral by the action of sulphuric acid. The tetrachlorinated ether distilled with sulphuric acid, also gives ethyl chloride and chloral:



Chloral is also formed when chlorine is passed into a cooled mixture of aldehyde and aqueous hydrochloric acid, or of aldehyde and water (Wurtz a. Vogt).

**Reactions and Combinations.** 1. Chloral is easily reduced to aldehyde by the action of nascent hydrogen evolved from an acid solution. If a solution of chloral hydrate be heated to  $50^\circ$  with zinc in a retort connected with a condenser cooled by ice, and very dilute acid gradually poured in, aldehyde will soon be obtained in quantity sufficient to admit of rectification, and identification by conversion into the ammonia compound. Polymeric modifications are formed at the same time, especially paraldehyde, which floats as an oily layer on the surface of the distillate (Persoune, *Compt. rend.* lxi. 227).

2. With phosphorus pentachloride chloral yields pentachlorethane,  $\text{C}^2\text{HCl}_5$  (1st Suppl. 432), and with the chlorobromide,  $\text{PCl}_3\text{Br}_2$ , it forms in like manner trichloro-dibromethane,  $\text{C}^2\text{HCl}_3\text{Br}_2$ . On adding water to the product of the reaction, an oil separates, which, when dried and submitted to fractional distillation under diminished pressure, yields the compound  $\text{C}^2\text{HCl}_3\text{Br}_2$  as a colourless, transparent, highly refracting liquid, of sp. gr. 2.317 at  $0^\circ$  having a pleasant odour, insoluble in water, but readily soluble in alcohol and ether. It boils at about  $200^\circ$  with partial decomposition, but distils unchanged at  $93^\circ$ – $95^\circ$  at a pressure of 14 millimeters. Its refractive index for D at  $25.7^\circ$  is 1.52991. When treated with alcoholic potash, it is rapidly decomposed, with formation of potassium chloride, and an oily substance distilling at  $143^\circ$ – $160^\circ$ , but apparently not homogeneous (Paternò, *Gazzetta chimica italiana*, i. 500).

3. With sulphuric acid.—Chloral mixed with fuming sulphuric acid solidifies, after a short time, to a white crystalline mass, which contains neither insoluble chloral nor chloralide, but has the composition  $\text{C}^2\text{H}^2\text{Cl}^2\text{S}^2\text{O}^{11}$ , which is that of an anhydride of neutral chloral sulphate formed by combination of 4 mol. chloral and 2 mol. sulphuric acid, with elimination of 1 mol. water:



This compound is not altered by cold water, but is readily decomposed by warm water, potassium hydrate, or alcohol, in the latter instance with formation of chloral alcoholate. From ether, in which it is very soluble, it crystallises in needles.

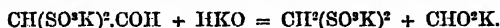
On passing the vapour of sulphuric anhydride into chloral, the whole solidifies to a mass of needles differing from the compound just described. It crystallises from alcohol apparently unchanged, is insoluble in cold water, but is decomposed by warm water and by a solution of potassium hydrate. When gently heated it melts, and separates into two layers, whilst at a higher temperature it evolves hydrochloric acid, and leaves an oil which does not solidify and is not acted upon by water (Grabowski, *Deut. Chem. Ges. Ber.* vi. 225).

4. A concentrated solution of chloral hydrate mixed in the cold with neutral potassium sulphite yields chloroform, potassium formate and a compound of chloral with acid potassium sulphite. But at a temperature approaching the boiling point the chlorine of the chloral is acted upon, and by adding the solution of the latter very gradually to the hot solution of the sulphite, to avoid loss of chloral by production of chloroform, then cooling and evaporating, there are obtained a diff. white salt,  $\text{CH}(\text{SO}^2\text{K})\text{COH.HKSO}_3 + \text{H}_2\text{O}$ , and a very soluble salt—



besides a little potassium formene-disulphonate (methionate),  $\text{CH}^2(\text{SO}^*\text{K})^2$ , potassium formate, chloride, sulphate, and hyposulphate.

The salt,  $\text{CH}(\text{SO}^*\text{K})^2.\text{COH}.\text{HKSO}^* + \text{H}_2\text{O}$ , crystallises in indistinct rhombic plates, but when it is dissolved in hot water, crystals containing more water always separate in the form of soft, brilliant white needles entangled together, and so minute that the whole appears amorphous. A cold supersaturated solution is, however, easily prepared, and on dropping a crystal of the original form into it, crystals of the same kind go on forming for a short time, though they are soon overgrown by the more hydrated crystals. This salt is the compound of acid potassium sulphite with potassium aldehyde-disulphonate, this latter constituent having the composition of chloral in which two atoms of chlorine are replaced by  $\text{SO}^*\text{K}$  and the third by hydrogen. Boiled with potassium carbonate, it yields—besides the neutral sulphite—formene-disulphonate and formate, the behaviour of the aldehyde-disulphonate  $\text{CH}(\text{SO}^*\text{K})^2.\text{COH}$  towards alkalis being in fact similar to that of chloral—



Lead peroxide gives the same salts together with lead sulphate.

On treating the cold solution of the double salt with bromine until it remains permanently coloured, the sulphite is oxidised, and potassium aldehyde-disulphonate,  $\text{CH}(\text{SO}^*\text{K})^2.\text{COH} + \text{H}_2\text{O}$ , is set free. A similar destruction of the double salt is effected by boiling it for half an hour with hydrochloric acid. By boiling the aldehyde-disulphonate with acid sulphite, the double salt can easily be reproduced. Potassium aldehyde-disulphonate can be heated to  $130^\circ$  without undergoing change, and loses its water of crystallisation but slowly at  $170^\circ$ – $175^\circ$ ; above this it decomposes, swelling up into an exceedingly bulky twisted mass like 'Pharaoh's serpents.' The barium salt,  $\text{CH}(\text{SO}^*\text{K})^2.\text{Ba}.\text{COH} + 2\text{H}_2\text{O}$ , forms slender needles, sparingly soluble in water, which can be recrystallised from hot acetic acid.

A solution of potassium aldehyde-disulphonate warmed with excess of bromine yields a much more soluble brominated salt,  $\text{CBr}(\text{SO}^*\text{K})^2.\text{COH}$ , which crystallises out in needles on evaporating and cooling the solution. It is decomposed by heat, leaving a residue of potassium bromide and sulphate mixed with a little carbon. Neither silver nitrate, barium chloride, nor baryta-water precipitates its solutions. When it is boiled for a few seconds with potassium sulphite, the original double salt,  $\text{CH}(\text{SO}^*\text{K})^2.\text{COH} + \text{HKSO}^* + \text{H}_2\text{O}$ , separates out again on cooling. Boiled for half an hour with potassium carbonate and neutralised with acetic acid, the tolerably concentrated solution, after heating with alcohol and cooling, gives a deposit of microscopic plates or needles of another brominated salt. This salt, when boiled for a few seconds with potassium sulphite, yields on cooling, crystals of  $\text{CH}^2(\text{SO}^*\text{K})^2$ ; it must therefore be  $\text{CHBr}(\text{SO}^*\text{K})^2$ , obtained, together with potassium formate, from  $\text{CBr}(\text{SO}^*\text{K})^2.\text{COH}$ , just as  $\text{CH}^2(\text{SO}^*\text{K})^2$  is obtained from  $\text{CH}(\text{SO}^*\text{K})^2.\text{COH}$ .

The second salt obtained by the action of potassium sulphite upon chloral, which is readily soluble in water, and has the complex formula above given, crystallises in large shining triclinic prisms, and can be obtained quite pure by repeated crystallisations from warm water. When heated, it swells up considerably, blackens, and leaves a residue of potassium sulphate and chloride and some carbon. Its water of crystallisation could not be directly determined, in consequence of decomposition taking place. It gives precipitates with silver and lead nitrates, soluble in nitric acid. Baryta-water precipitates barium sulphite from its solutions, the salts  $\text{CCl}(\text{SO}^*\text{K})^2.\text{COH}$  and  $\text{CHCl}(\text{SO}^*\text{K}).\text{COH}$  being doubtless left in solution; but these salts have not been obtained in the pure state, only a syrupy liquid being formed on evaporation. This, however, on treatment with acid potassium sulphite, reproduces the crystalline double salt. Either component of this double salt would, by further action of potassium sulphite, produce the salt,  $\text{CH}(\text{SO}^*\text{K})^2.\text{COH} + \text{HKSO}^*$ , by replacement of  $\text{Cl}$ , in the one case by  $\text{H}$  and in the other by  $\text{SO}^*\text{H}$ ; so that the tendency to produce the salt  $\text{H}(\text{SO}^*\text{K})^2.\text{COH}$  appears to be fulfilled in two distinct ways so far as regards the stages of the process.

It is remarkable that the two components of the double salt are produced in the proportion to form it, no excess of either being found in the mother-liquor. The reluctance therefore that the two only compounds intermediate between chloral and potassium aldehyde-disulphonate which can result from the replacement of two atoms chlorine, can unite to form a double salt, actually occasions both of them to be produced in a perfectly definite proportion.

During the digestion of chloral hydrate with potassium sulphite, a strong penetrating smell is given off, quite distinct from that of either chloroform or chloral, some of

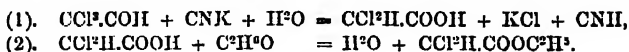
the chloral being apparently converted into mono- and dichloraldehyde. A very large quantity of it appears to be changed into these or other volatile bodies (Rathke, *Ann. Ch. Pharm.* clxi. 149).

5. Chloral digested with *hydrochloric* and *hydrocyanic acid* in aqueous solution, unites with the latter, forming chloral hydrocyanide,  $C^2HCl^2O.CHN$ , or,  $CCl^2-CH(OH)(CN)$ , which crystallises in prisms united in white cauliflower-like groups. It has a pungent bitter taste, dissolves easily in water, alcohol and ether, and when digested with moderately strong hydrochloric acid, yields sal-ammoniac and trichlorolactic acid,  $CCl^2-CH\begin{matrix} OH \\ \diagup \\ COOH \end{matrix}$  (Bischoff u. Pinnor, *Deut. Chem. Ges. Ber.* v. 113).

According to Hagemann (*ibid.* 151) chloral hydrocyanide is precipitated from watery solutions in oily drops by strong sulphuric acid, or fuming hydrochloric acid. It melts at  $58^{\circ}-59^{\circ}$ , solidifies at  $57.5^{\circ}-58^{\circ}$ , begins to boil at  $120^{\circ}$ , with partial decomposition, the greater part passing over at  $140^{\circ}-145^{\circ}$ .

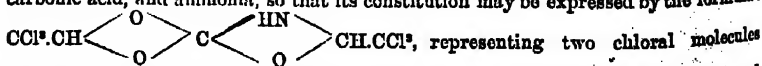
Chloral hydrate, hydrocyanic acid, and fuming hydrochloric acid, heated for 4-5 hours in sealed tubes to  $120^{\circ}-130^{\circ}$ , gave, after the ammonium chloride had been removed, alcohol, a zinc salt of trichlorolactic acid (Hagemann).

6. When 1 mol. chloral hydrate is added to 1 mol. *potassium cyanide* under absolute alcohol, a powerful reaction sets in, accompanied by an abundant evolution of hydrocyanic acid. On adding water to the product, a heavy oil separates, from which, by repeated fractional distillation, ethyl dichloracetate, boiling between  $154^{\circ}$  and  $157^{\circ}$ , may be obtained; also, in the higher portion, a solid crystalline substance melting at  $62^{\circ}$ , and apparently identical with the chloral-hydrocyanide above described. When the dilute alcoholic solution mentioned above, from which the oil had been separated, is evaporated to dryness at  $100^{\circ}$ , and exhausted with absolute alcohol, it yields potassium dichloracetate, crystallising from the alcohol in large plates. When potassium cyanide and chloral hydrate react on one another in presence of water, hydrocyanic acid is evolved, and free dichloroacetic acid obtained, only a small amount of potassium dichloracetate being produced, and that being probably due to the presence of potassium hydrate or carbonate in the potassium cyanide employed. The reactions which take place may therefore be represented as follows:



When a solution of chloral hydrate in benzene is added to potassium cyanide, the reaction is somewhat different, hydrocyanic acid being evolved, and scarcely anything but chloral hydrocyanide being formed. On the other hand, if solid chloral hydrate be added to potassium cyanide under benzene, but little chloral hydrocyanide is produced, the benzene on spontaneous evaporation leaving microscopic prismatic crystals, melting at  $123^{\circ}$ , and having the composition  $C^2H^2Cl^2O^2N$ . This compound splits up on distillation into chloral and chloralide, melting at  $112^{\circ}-114^{\circ}$  (Wallach, *Deut. Chem. Ges. Ber.* vi. 114).

7. Vapour of *cyanic acid* is readily absorbed by chloral, which sometimes solidifies at the moment of saturation; at other times, gas is evolved at a certain stage of the process, and the mixture solidifies immediately, or after some time, to a vitreous mass like fused borax. The product, however, in all instances, yields the same result when boiled with moderately concentrated hydrochloric acid, leaving a white granular powder, insoluble in water and in hydrochloric acid. This, however, is readily soluble in hot alcohol, and even more so in ether, from which it crystallises in microscopic prisms having the composition  $C^2H^2Cl^2NO^2$ , and melting at  $167^{\circ}-170^{\circ}$ , with partial decomposition. Boiled with potassium hydrate, it yields chloroform, formic acid, carbonic acid, and ammonia, so that its constitution may be expressed by the formula:



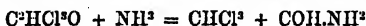
united by cyanic acid. On heating it to  $200^{\circ}$ , it splits up, chloral distilling over, and cyanamide being formed. It dissolves readily in alcoholic ammonia, and after removal of the excess of the latter, silver nitrate gives a precipitate of silver cyanate. The hydrochloric acid solution of the crude substance, after separation of the compound above described, yielded on evaporation, besides ammonium chloride, two distinct crystalline compounds, the quantity of which, however, was too small to admit of accurate examination (G. Bischoff, *Deut. Chem. Ges. Ber.* v. 86).

8. When dry *ammonia gas* is slowly passed into a small quantity (not more than 2 or 3 grams) of anhydrous chloral cooled to a very low temperature, great heat is

evolved and chloral-ammonia,  $\text{C}^2\text{HCl}^3\text{.NH}^3$ , analogous to aldehyde-ammonia, is formed, as a white, fusible, volatile body having the odour of aldehyde-ammonia. This compound is decomposed by strong sulphuric acid into chloral and ammonium sulphate, and by water into chloroform and ammonium formate:

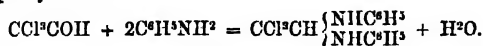


If more than 2 or 3 grams of substance is used for the preparation of chloral-ammonia, there is always obtained, as secondary product, a syrupy mass, resolvable by distillation into chloroform, and a residue which yields hydrocyanic acid when distilled with phosphoric anhydride, and therefore appears to be formamide:



(Personne, *Compt. rend.* lxxi. 22).

9. Chloral unites also with *Amines and Amides*.—With *aniline* it forms trichlor-ethylidene-diphenylamine  $\text{C}^1\text{H}^3\text{Cl}^3\text{N}^2$ , a crystallised body analogous to Schiff's ethylidene-diphenylamine:



This compound melts at  $100^\circ$ – $101^\circ$ , but soon begins to decompose when kept at this temperature. It is insoluble in water and decomposes when boiled with water or alcohol, evolving a penetrating odour like that of phenylisocyanide. Treated with acids it undergoes decomposition, yielding salts of aniline. It does not, therefore, appear to possess basic properties. Hydrochloric acid gas passed into its solution in benzene gives rise to the formation of a large quantity of aniline hydrochloride, and an oily body which has not as yet been obtained in a state fit for analysis.

*Toluidine* acts upon chloral in the same manner as aniline, giving rise to trichlor-ethylidene-ditoluylamine,  $\text{CCl}^3\text{CH} \begin{Bmatrix} \text{NHC}^6\text{H}_4\text{CH}_3 \\ \text{NHC}^6\text{H}_4\text{CH}_3 \end{Bmatrix}$ , a crystalline body which melts at  $114^\circ$ – $115^\circ$ . When alcohol is added to the crude product of the reaction before cooling, large crystals of the compound  $\text{CCl}^3\text{CH} \begin{Bmatrix} \text{OC}^6\text{H}_5 \\ \text{NHC}^6\text{H}_4\text{CH}_3 \end{Bmatrix}$  are obtained, melting at  $76^\circ$ – $77^\circ$  (Wallach, *Deut. Chem. Ges. Ber.* v. 251).

Chloral also unites with *acetamide* and *benzamide*. Chloral-acetamide  $\text{C}^2\text{HCl}^3\text{O.C}^2\text{H}^3\text{ON}$  is a crystalline compound melting at  $156^\circ$ – $157^\circ$ , yielding by distillation, first chloral, then acetamide, and leaving a black residue. With aqueous alkalis it gives chloroform, ammonia, and acetate and formate of the alkali-metal. Chloral-benzamide  $\text{C}^2\text{HCl}^3\text{O.C}^6\text{H}_5\text{ON}$  melts at  $150^\circ$ – $151^\circ$ , and is decomposed by alkalis in a similar manner to the preceding compound (Wallach, *loc. cit.*; Jacobsen, *Ann. Ch. Pharm.* clvii. 243).

On adding chloral to a saturated solution of *urea*, combination takes place, the compound  $\text{C}^2\text{HCl}^3\text{O.CO.H}^2\text{N}^2$  being formed when the urea is in excess, and  $2\text{C}^2\text{HCl}^3\text{O.CO.H}^2\text{N}^2$  when the chloral is in excess. The latter body is also formed by heating dry urea with chloral to  $100^\circ$  (Jacobsen).

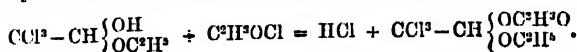
**Chloral Hydrate**,  $\text{C}^2\text{HCl}^3\text{O.H}^2\text{O}$ .—This compound is formed by the direct combination of chloral and water. The crystalline substance formed by the action of chlorine on absolute alcohol has usually been regarded also as chloral hydrate; but Personne, Lieben, and others, have shown that the ultimate product of this reaction is not the hydrate but the alcoholate of chloral,  $\text{C}^2\text{HCl}^3\text{O.C}^2\text{H}^5\text{O}$  (p. 313).

According to Flückiger (*Zeitschr. f. Chem.* vi. 432) the best method of purifying chloral hydrate is to recrystallise it from pure carbon sulphide, which takes up about  $\frac{1}{4}$  of its weight of chloral at  $15^\circ$ – $18^\circ$ , and from  $\frac{1}{2}$  to  $\frac{1}{4}$  at the boiling heat. From the hot saturated solution the excess of chloral hydrate separates in beautiful prisms, which, on exposure to the air, quickly give off the solvent remaining attached to them. Chloral hydrate thus purified boils at  $97.5^\circ$  (thermometer wholly in the vapour).

According to Phipson (*Chem. News*, xxv. 257) pure chloral hydrate crystallises in oblique rhombic prisms, sometimes shortened in such a manner as to give them the appearance of acute rhombohedrons. The solution of the crystals in water is attended with considerable fall of temperature, whereas the formation of the solid hydrate by combination of chloral and water is attended with considerable evolution of heat. Half a pound of the hydrate mixed rapidly with half a pound of water, causes the thermometer to sink many degrees below  $0^\circ$ . Minute fragments of the crystals floating on the surface of pure distilled water move about rapidly with the peculiar gyratory motion exhibited under similar circumstances by camphor.

**Constitution of Chloral Hydrate.** To decide whether this body is a true diatomic alcohol (trichlorethylidene glycol)  $\text{CCl}^3\text{.CH(OH)}^2$ , or merely a compound of chloral with

water of crystallisation  $\text{CCl}_3\cdot\text{CHO} + \text{H}_2\text{O}$ , Meyer a. Dulk (*Deut. Chem. Ges. Ber.* iv. 963) have subjected it to the action of acetyl chloride, whereby they obtain tetrachlorinated ethyl acetate  $\text{CCl}_3-\text{CH}(\text{Cl})\text{OC}_2\text{H}_5\text{O}$ . Now chloral alcoholate treated in like manner yields the alcoholate of acetyl-chloral, according to the equation :



These results lead to the inference that chloral alcoholate is the ethylic ether of trichlorethylidene glycol; and therefore chloral hydrate as that glycol itself.

When perfectly anhydrous chloral and acetic anhydride are heated together to the temperature of  $150^\circ$  in molecular proportions, they unite, forming diacetyl chloral

hydrate  $\text{CCl}_3-\text{CH}(\text{O.C}_2\text{H}_3\text{O})_2$ , which boils constantly at  $221^\circ-222^\circ$  (uncorrected),

has a sp. gr. of 1.422 at  $11^\circ$ , is not miscible with water, and is not attacked by cold potash-solution, though, on heating it, the odour of chloroform is perceptible; it is evidently trichlorinated diacetate of ethylidene glycol, the diacetate itself being similarly obtained by heating aldehyde and acetic anhydride to  $180^\circ$  as shown by Geuther (*Ann. Ch. Pharm.* cvi. 249).

When chloral hydrate is heated with five times its weight of syrupy glycerin, reaction begins at  $100^\circ$  and goes on to  $230^\circ$ , a distillate being obtained consisting of chloroform; formic acid, and undecomposed chloral hydrate, together with hydrochloric acid and allyl formate as secondary products (H. Byasson, *Compt. rend.* lxxv. 1628).

**Valuation of Chloral Hydrate.**—The quality of commercial chloral hydrate is usually tested by decomposing it with ammonia or a fixed alkali, and measuring or weighing the quantity of chloroform thereby set free. C. H. Wood (*Pharm. J. Trans.* [3] i. 703) recommends boiling the hydrate in aqueous solution with lime (which has no sensible action on chloroform) and distilling off the chloroform produced. To ascertain whether the hydrate contains any alcoholate, the aqueous portion of the distillate may be tested for alcohol with the iodoform test.

The decomposition with alkalis does not, however, afford perfectly accurate results, as some chloroform is taken up by the water, and some water dissolved by the chloroform. For this reason Versmann (*Pharm. J. Trans.* [3] i. 701, 965) prefers decomposing the chloral hydrate with sulphuric acid: 5 to 6 c.c. concentrated sulphuric acid are put into a graduated, well-stopped tube, and heated by placing the tube in water at  $60^\circ$ ; 10 grams chloral hydrate are then added, the whole well shaken, and the tube put back into the hot water. The decomposition is instantaneous, and the anhydrous chloral floating on the acid may be read off as soon as the liquid has cooled down. By about twelve hours standing metachloral is produced. In comparative experiments a somewhat higher result is always given by sulphuric acid than by ammonia. In working with 10 grams of chloral hydrate by the ammonia-test, there is, in fact, a constant loss of 0.2 c.c. of chloroform, owing to the solubility of the latter in water; if, however, the necessary correction be made for this loss, the result will agree with that obtained by the sulphuric acid test.

On the quality and valuation of commercial chloral hydrate, see also C. Müller (*Zeitschr. f. Chem.* [2] vii. 66; *Chem. Soc. J.* [2] ix. 444; *Chem. News*, xxiii. 113); Paul (*Pharm. J. Trans.* [3] i. 621; *Chem. Soc. J.* [2] ix. 134).

On the physiological action of chloral hydrate see Byasson (*Compt. rend.* lxxii. 742; *Chem. Soc. J.* [2] ix. 748). On its use as an antiseptic, *Dingl. polyt. J.* cxiv. 280.

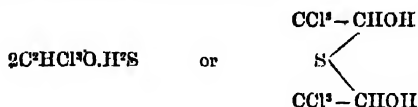
**Chloral Sulphydrates.**—(1.)  $\text{C}_2\text{HCl}_3\text{O.H}^2\text{S} = \text{CCl}_3 - \text{CH}(\text{OH})\text{SH}$ . Anhydrous

chloral readily absorbs hydrogen sulphide, and after the action of the gas has been continued for about twenty-four hours, the whole solidifies to a white crystalline mass. This may be purified by distillation and subsequent crystallisation from ether or from absolute alcohol, whereby it is obtained in rhomboidal plates or quadrangular prisms, having the composition above given. Chloral sulphydrate has a disagreeable odour and characteristic taste, resembling that of chloral hydrate. It melts at  $77^\circ$  and boils at  $123^\circ$ . It is soluble in all proportions in anhydrous alcohol, ether, or chloroform, but is decomposed by water, with deposition of sulphur, the action being very complex. Alkaline solutions yield chloroform and an alkaline formate and sulphydrate. Nitric acid oxidises it, with formation of trichloroacetic acid. Sulphuric acid has no action on it in the cold, but when heated with it produces anhydrous chloral, whilst sulphuretted hydrogen and sulphurous anhydride are evolved and sulphur is deposited.



The physiological action of this compound is very similar to that of chloral hydrate. .2 to .3 gram administered to guinea-pigs, by subcutaneous injection of the ethereal solution, produced deep sleep and a slight acceleration of the movements of the heart (Byasson, *Compt. rend.* lxxiv. 1290).

(2) Hydrogen sulphide passed into an ethereal solution of anhydrous chloral, forms a number of compounds, only one of which has yet been isolated. This body has the composition



It is insoluble in water, soluble in ether and in alcohol. The alcoholic solution treated with lead acetate, yields lead sulphide and chloral hydrate (Hagemann, *Deut. Chem. Ges. Ber.* v. 154).

**Chloral Alcoholate**,  $\text{C}^2\text{HCl}^3\text{O} \cdot \text{C}^2\text{H}^4\text{O} = \text{CCl}^3 - \text{CH} \begin{Bmatrix} \text{OH} \\ \text{OC}^2\text{H}^5 \end{Bmatrix}$ . This compound is formed by direct combination of anhydrous chloral with absolute alcohol, and is also the final product of the action of chlorine on absolute alcohol. Roussin (*Compt. rend.* lxxix. 1144); *Jahresber.* 1860, 504) obtained by this latter process a crystalline product melting at  $56^\circ$  and boiling at  $115^\circ$ , which he supposed to be chloral hydrate. J. Thomsen (*Deut. Chem. Ges. Ber.* ii. 597) also regarded the product thus obtained as chloral hydrate. Personne, however (*Compt. rend.* lxxix. 1363), has shown that it is not the hydrate, but the alcoholate of chloral, inasmuch as it gives by analysis only 34.9 p. c. chlorine (the hydrate requiring 64.3 p.c.), and when distilled with potash, yields alcohol as well as chloroform.

Lieben also (*Deut. Chem. Ges. Ber.* iii. 907) finds that the ultimate product of the action of chlorine on absolute alcohol has exactly the composition of chloral alcoholate; it melts at  $43^\circ$ – $40^\circ$ , and boils at  $114^\circ$ – $115^\circ$ . Its vapour-density, determined by Dumas' process between  $157^\circ$  and  $198^\circ$ , was found in two experiments to be 3.68 and 3.49; now the formula  $\text{C}^2\text{H}^2\text{Cl}^3\text{O}^2$  calculated for a condensation to 2 volumes requires 6.08; hence it appears that the alcoholate is resolved at high temperatures into its components.

According to Lieben, the alcoholate may perhaps be produced from previously formed trichloroacetal, according to the equation:



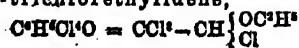
It is possible also that dichloroacetal, formed by the action of chlorine on the alcohol, may be converted, by an analogous reaction, into the mono-ethylin  $\text{HO}(\text{C}^2\text{H}^2\text{Cl}^3)\text{OC}^2\text{H}^5$ , which, by further action of chlorine, is converted into chloral alcoholate.

Lastly, the question as to the composition of the crystalline product of the action of chlorine on alcohol has been examined by Jungfleisch, Lebaigue a. Roucher (*J. Pharm.* [4] xi. 208), who were commissioned by the *Société de Pharmacie* in Paris, to undertake the enquiry. For this purpose they prepared by synthesis pure chloral hydrate (I.), and pure chloral alcoholate (II.), and compared these preparations with chloral hydrate prepared by Personne (P), with a sample of the hydrate prepared in Germany and sold under Liebreich's guarantee (L), and with a product prepared by Roussin (R). The results of the comparison show clearly that Roussin's product is the alcoholate, and not the hydrate.

	I.	P.	L.	II.	R.
Boiling point (corr.)	97	97	97.5	113.5	113.5
Sp. gr. at $66^\circ$ of the liquid substance	1.5704	1.5771	1.5719	1.3439	1.3286.

According to C. A. Martius and P. Mendelssohn-Bartholdy (*Deut. Chem. Ges. Ber.* iii. 443) chloral hydrate boils at  $95^\circ$ , the alcoholate at  $115^\circ$ – $116^\circ$ , and solidifies at  $40^\circ$  to a radio-crystalline mass. Its specific gravity at  $40^\circ$  in the fused state is 1.143. It dissolves easily in alcohol, ether, ethyl acetate, and light petroleum oils, and separates on cooling from the warm ethereal solution in long needles.

When chloral alcoholate is gently heated with phosphorus pentachloride (1 mol. of each), torrents of hydrochloric acid are evolved, the pentachloride disappears, and on adding water to the product to decompose phosphorus oxychloride, tetrachlorethyl oxide or chloroethyl-trichlorethylidene,



separates out as a heavy colourless oil, which boils without decomposition at  $188^{\circ}$ , is insoluble in water, has a pungent camphorous smell, and a sweetish bitter taste, and is decomposed by boiling potash, like chloral, yielding chloroform.

This compound is intermediate between trichloroacetal  $\text{CCl}_3 - \text{CH}(\text{OC}^2\text{H}^5)_2$  boiling at  $230^{\circ}$ , and trichloroethylidene dichloride  $\text{CCl}_3 - \text{CHCl}_2$  boiling at  $158^{\circ}$ . Its existence throws further light on the constitution of the hydrate and alcoholate of chloral. For if the latter were a molecular compound in which the chloral and alcohol existed as such, it ought to yield with phosphorus pentachloride the same products as are obtained from those bodies separately, viz.  $\text{CCl}_3 \cdot \text{CHCl}_2$  and  $\text{C}^2\text{H}^5\text{Cl}$ . But if chloral alcoholate is a real atomic compound, namely, the monothylic ether of trichloroethylidene glycol,  $\text{CCl}_3 - \text{CH} \begin{Bmatrix} \text{OC}^2\text{H}^5 \\ \text{OH} \end{Bmatrix}$ , the action of phosphorus pentachloride on chloral alcoholate must give rise to the replacement of OH by Cl yielding, as actually observed, the body  $\text{CCl}_3 - \text{CH} \begin{Bmatrix} \text{OC}^2\text{H}^5 \\ \text{Cl} \end{Bmatrix}$ . The alcoholate and hydrate must therefore be regarded as atomic compounds, the latter being the glycol of trichloroethylidene (p. 312).

The boiling points of the hydrate ( $95^{\circ}$ ) and of the alcoholate ( $115^{\circ}$ ) should, according to analogy, be higher than that of the compound  $\text{CCl}_3 - \text{CHCl}(\text{OC}^2\text{H}^5)$ ; but these temperatures, as shown by the vapour-density determinations, are not the real boiling points, but temperatures at which the compounds in question suffer decomposition. The decomposition of chloral hydrate into water and chloral is quite analogous to the decomposition of secondary alcohols, such as amylene hydrate into water and an olefine (L. Henry, *Deut. Chem. Ges. Ber.* iv. 101, 435; *Chem. Soc. J.* [2] ix. 255, 696).

The constitution of chloral alcoholate is further established, as already observed (p. 312), by its reaction with acetyl chloride, the product of which is acetyl-chloral alcoholate or the ethyl-acetic ether of trichloroethylidene glycol  $\text{CCl}_3 - \text{CH} \begin{Bmatrix} \text{OC}^2\text{H}^5 \\ \text{OC}^2\text{H}^3 \end{Bmatrix}$ . This compound, purified by repeated fractional distillation, is a colourless transparent oil, having a peculiar odour, boiling constantly at  $198^{\circ}$  (uncorr.), and of sp. gr. 1.327 at  $11^{\circ}$ . It is not attacked by aqueous potash at the boiling heat.

**Homologues of Chloral Alcoholate** (Mendelssohn-Bartholdy a. Martius, *Deut. Chem. Ges. Ber.* iii. 443; Jacobsen, *Ann. Ch. Pharm.* clvii. 243). Chloral unites with the homologues of ethyl alcohol, forming crystalline compounds very similar to the ordinary alcoholate. They are decomposed by strong sulphuric acid with production of chloral.

The *methyl-compound*,  $\text{CCl}_3 - \text{CH}(\text{OH})(\text{OCH}^3)$ , forms a crystalline somewhat hygroscopic mass, very much like the ethyl-compound, melting at  $50^{\circ}$ , boiling at  $160^{\circ}$  (Jacobsen), at  $98^{\circ}$  (Bartholdy a. Martius).

The *amyl-compound*,  $\text{CCl}_3 - \text{CH}(\text{OH})(\text{OC}^4\text{H}^{11})$ , crystallises in long, very beautiful needles, nearly insoluble in water, easily soluble in alcohol and ether, melting at about  $56^{\circ}$ , boiling at  $145^{\circ}$ – $147^{\circ}$ . It is not decomposed by heating with water, but sinks to the bottom as a heavy layer, which solidifies under the liquid only at very low temperatures (Jacobsen). According to Bartholdy a. Martius, it boils at  $143^{\circ}$  and has a specific gravity of 1.2340 at  $25^{\circ}$ . It solidifies at  $25^{\circ}$  to a crystalline mass, easily soluble in alcohol, ether, and light petroleum oil, from which last solvent it crystallises in tufts of long needles. By prolonged boiling with water, it is resolved into amyl alcohol and chloral (hydrate).

The *cetyl-compound*,  $\text{CCl}_3 - \text{CH}(\text{OH})(\text{OC}^{18}\text{H}^{37})$ , is obtained in soft warty groups of microscopic needles, when cetyl alcohol is dissolved in a slight excess of warm chloral, and the solution is left to cool slowly (Jacobsen).

*Chloral Mercaptide*,  $\text{CCl}_3 - \text{CH}(\text{OH})(\text{SC}^2\text{H}^5)$ , formed by the combination of chloral with ethyl sulphhydrate, dissolves easily in alcohol, ether, and carbon sulphide, and may be crystallised therefrom (Bartholdy a. Martius).

The alcohols of the aromatic series do not unite with chloral (Jacobsen).

**CHLORATES.**—*Barium Chlorate*,  $\text{Ba}(\text{ClO}^3)_2$ . Widemann prepares this salt by heating a mixture of 1 mol. crystallised aluminium sulphate, 1 mol. sulphuric acid, and 2 mols. potassium chlorate with a quantity of water, sufficient to give it a thin, pasty consistence. Crystallised potash-alum then separates on cooling, while chloric acid remains dissolved. A four-fold volume of water is then added, and the liquid, after filtration, is neutralised with baryta-water, whereupon barium sulphate separates out, together with a little more alum. The liquid is again filtered, the greater part of the alcohol removed, and the liquid, after a second filtration, is evaporated to the crystallising point (*Arch. Pharm.* [2] cxliv. 66).

**Potassium Chlorate,  $\text{KClO}_3$ .** A method of preparing this salt on the large scale is described by W. Hunt (*Dingl. polyt. J.* ccc. 77). Diluted chlorine gas is passed into a brick tower, into which there also drops a solution of potassium chloride and milk of lime. The potassium chlorate thus formed is separated by crystallisation.

**Decomposition by heat.**—It is well known that the decomposition of potassium chlorate by heat is greatly facilitated by mixing it with various metallic oxides, as manganese dioxide, or cupric oxide in the state of powder; but the manner in which these substances act has not been very clearly made out. G. Hornsby (*Pharm. J. Trans.* xv. 352), maintained that oxygen, disengaged from potassium chlorate in presence of manganese dioxide, is always accompanied by chlorine, with production of a brilliant and intermittent light, which he attributed to electricity, engendered by the molecular change of the gaseous particles. On the other hand, Witt (*ibid.* 411) maintained that the oxygen obtained from such a mixture at a high temperature possesses much more combustible energy than the same gas prepared at a low temperature; and that the sparks observed by Hornsby were due to organic matters which, by chance, were in contact with the gas. Witt also recalls the two phases of the decomposition of potassium chlorate originally observed by Sérrullas, and confirmed by Millon:



and observes that the oxygen produced in the second stage of the reaction is much more active than that produced in the first stage, as, like ozone, it turns iodised test-paper blue. The same character is also met with in the oxygen prepared from potassium chlorate by the aid of manganese dioxide, although he further supposes that this oxide exerts a purely mechanical action, interposing itself between the particles of the chlorate, and thus facilitating its decomposition by heat, just as certain powders thrown into heated liquids facilitate their ebullition. The same kind of action is exerted by the oxides of copper, iron, and chromium, none of these bodies undergoing any change whatever. A similar view was subsequently put forward by Deville (*Leçons sur la Dissociation, professées à la Société chimique*, 1864, p. 353), who compares the decomposition of potassium chlorate by heat to the ebullition of water charged with a salt, the solution becoming concentrated as the vapour escapes. Here the vapour is oxygen and the potassium chloride produced becomes the salt which is concentrated. On adding a foreign body, oxide of copper, oxide of manganese, &c., to the chlorate in fusion, these auxiliaries of ebullition evidently favour the disengagement of oxygen, as they would favour in water the production of vapour. This view is, however, at variance with the fact that potassium chlorate loses its oxygen without entering into fusion.

E. O. Brown (*Pharm. J. Trans.* xv. 460) impugns this theory, and considers that the oxide of manganese acts by its proper nature, inasmuch as the same effect is not produced by the presence of other finely divided substances, powdered quartz for example. He attributes the supposed activity of the gas obtained under these circumstances to the presence of chlorine. Witt, however (*ibid.* 503), finds that the same or even greater activity is exhibited by oxygen evolved from substances not containing chlorine, namely, from a mixture of potassium dichromate and sulphuric acid.

Schönbein (*Jahresb.* 1855, 269; 1857, 62) suggested that potassium chlorate may be regarded as a compound of potassium chloride and ozone, and that this ozone is converted, by the combined active oxygen of the manganese dioxide, &c., into ordinary oxygen, which can then no longer remain united to the potassium chloride.

This view is controverted by Wiederhold (*Pogg. Ann.* cxvi. 171) on the ground that platinum black facilitates the decomposition of potassium chlorate, as well as bodies containing oxygen, and that the oxygen thus evolved turns iodised starch-paper blue, whence it cannot be ordinary oxygen. An intimate mixture of 2 pts. potassium chlorate with 1 pt. manganese dioxide begins to give off oxygen at  $200^\circ$ – $206^\circ$ ; with cupric oxide, the evolution of gas begins at  $230^\circ$ – $235^\circ$ , with platinum-black at  $260^\circ$ – $270^\circ$ , with lead dioxide at  $280^\circ$ – $285^\circ$ . Wiederhold attributes the action of these several substances to their power of absorbing heat; the relative volume of the catalytic substances appears also to be of some importance, inasmuch as those bodies which induce the decomposition at the lowest temperature are also the most bulky. When a mixture of manganese dioxide and potassium chlorate is heated for some time to  $200^\circ$ , the evolution of oxygen ceases, recommencing only at a higher temperature; then ceasing again, and so on by steps up to  $260^\circ$ ; but when the mixture of potassium chlorate with manganese dioxide or cupric oxide is quickly heated to  $280^\circ$ – $290^\circ$ , a very tumultuous evolution of oxygen is set up, the temperature of the mixture rising at

once through  $40^{\circ}$  or  $50^{\circ}$ ; in the other mixtures the tumultuous evolution of gas does not take place till the heat is raised above  $340^{\circ}$ . During the heating of these mixtures, the temperature of the middle of the mass is always considerably below that of the external portions, uniformity of temperature being established after some time only; but when the mixture of potassium chlorate and manganese dioxide is heated to  $250^{\circ}$ , the temperature in the interior finally rises to  $254^{\circ}$ - $255^{\circ}$ , so that an actual evolution of heat takes place. The same rise of temperature is observed in a mixture of potassium chlorate and cupric oxide at  $290^{\circ}$ . Since cupric oxide and manganese dioxide do not exhibit this rise of temperature when heated alone, Wiederhold attributes the excess of temperature to the evolution of heat accompanying the liberation of the oxygen. It is further to be observed, that when potassium chlorate is decomposed in contact with any of these substances, no perchlorate is formed.

When potassium chlorate is heated to fusion, then removed from the fire, and small quantities of pulverised manganese dioxide, cupric oxide, &c., are thrown into it, evolution of oxygen begins immediately, the temperature rising to incandescence (at least with cupric oxide, and with ferric oxide or manganese dioxide prepared in the wet way). The manganese dioxide does not lose any oxygen. When 0.1 gram of the catalytic substance was added to 3 grams of potassium chlorate, complete decomposition was produced by cupric oxide, and by ferric oxide and manganese dioxide prepared in the wet way; with lead dioxide, native manganese dioxide, and platinum black, on the other hand, it was only partial.

Further experiments on this subject have recently been made by Baudrimont (*J. Pharm.* [4] xiv. 81, 161) whose results agree in the main with those of Wiederhold. By heating in a mercury-bath a mixture of 4 pts. pure and finely pulverised potassium chlorate with 1 pt. of black copper oxide prepared in the wet way, he finds that in presence of copper oxide, potassium chlorate can give up its oxygen at  $150^{\circ}$  or  $160^{\circ}$  below its normal temperature of decomposition (about  $400^{\circ}$ ), the disengagement of gas taking place easily and rapidly, and becoming tumultuous at about  $300^{\circ}$ , the temperature then rising suddenly to  $390^{\circ}$  without any sign of ignition. The whole of the oxygen of the chlorate is given off, together with a small quantity of chlorine, while the copper oxide is not altered in any way. Similar results were obtained with manganese dioxide. When the mixture of potassium chlorate and copper oxide was introduced into a platinum crucible previously heated nearly to dull redness, it fused, boiled quietly, then more quickly, with intumescence, and soon afterwards the decomposition was terminated by a general incandescence, leaving the crucible at a heat below redness.

The following experiments relate to the influence of various circumstances on the manner of the decomposition.

*Influence of the Nature of the Body in contact.*—The results are from experiments made upon 4 grams of potassium chlorate and 1 gram of the substance added. *Spongy Platinum.*—No action whatever up to  $360^{\circ}$ . When the two substances are fused together, the evolution of oxygen may be a little accelerated, but there is no incandescence. This result does not agree with Deville's theory. *Mercuric oxide.*—No action whatever up to  $360^{\circ}$ , the oxide being found intact after the operation. *Silver oxide.*—Gas is evolved at  $220^{\circ}$ , due however to the decomposition of the oxide. This soon ceases, and there is no further reaction even at  $360^{\circ}$ . Heated more strongly, the chlorate decomposes quietly, with formation of silver chloride and potassium oxide. This result is opposed to the statements of Schönbein and Witt, who say that the action of this oxide upon the chlorate is very energetic. *Potassium permanganate.*—Gas is slowly evolved at  $360^{\circ}$ , and the decomposition of the two salts proceeds simultaneously. The permanganate decomposes at about  $250^{\circ}$  into oxygen, potassium oxide and manganese sesquioxide; the last-named substance then reacts upon the chlorate, and gradually transforms it into potassium chloride and oxygen; the temperature not rising beyond  $360^{\circ}$ . *Black oxide of Copper.*—Result already given (*vid. sup.*). *Native Manganese dioxide.*—Sensible action, even before  $200^{\circ}$ , becoming continuous about  $250^{\circ}$ , and even violent about  $310^{\circ}$ - $320^{\circ}$ , the thermometer rising beyond  $380^{\circ}$ . The loss in weight is 1.62 grams, the excess over the calculated loss, 1.66 grams, being due to the evolution of a little chlorine. *Ferric oxide.*—Action begins about  $250^{\circ}$ , but is not continuous until  $320^{\circ}$ - $325^{\circ}$ . The evolution takes place readily, but there is no sudden rise of temperature, and the total decomposition of the salt requires a long time. *Black oxide of Cobalt, Brown oxide of Manganese, Dioxide of Lead.*—Action more feeble than with the substances previously named. A long time is necessary for the evolution of all the oxygen, and the temperature does not pass beyond  $360^{\circ}$ . The composition of these bodies undergoes no change during the reaction. All the preceding mixtures undergo true fusion when

the temperature rises to  $360^{\circ}$ . The weaker the action of the oxide, the less is the amount of chlorine evolved with the oxygen. *Alumina*.—Gas is evolved from  $250^{\circ}$ , but so much contaminated with chlorine, that the alumina appears to act as an acid. After the reaction the residue is alkaline, and the amount of potassium chloride present is 2.19 grams, instead of 2.44 grams, as required by theory.

*Influence of the State of Division of the Substances*.—Potassium chlorate is decomposed in presence of cupric oxide, with much greater facility when the salt is finely sifted than when it is only coarsely pulverised. 5 grams of a mixture of coarsely pulverised chlorate with one-tenth of its weight of cupric oxide, lost only 0.60 gram of oxygen at  $360^{\circ}$  whilst in a similar experiment with the salt finely sifted, the loss was 1.88 grams. But the influence of the state of the bodies is more plainly seen by comparing the effect of black copper oxide obtained in the moist way, with that obtained by ignition. The former decomposes the salt with great facility, and produces incandescence of the mixture when present to the extent of one two-hundredth part; while the latter acts only towards  $310^{\circ}$ – $320^{\circ}$ , causing a very slow and feeble evolution of gas, and scarcely producing incandescence when present as a twentieth part. So also manganese dioxide and ferric oxide obtained in the moist way, act with much greater facility than native manganese dioxide and ferric oxide obtained by ignition.

*Influence of the Proportion of the Active Substances as compared with the Amount of Potassium Chlorate*.—By experiments with black copper oxide, manganese dioxide, and ferric oxide, in proportions varying from one half to one five-hundredth part of the mixture, it was found that, although the decomposition of the chlorate is accelerated by even so small a proportion of the active substance as one five-hundredth part, yet the greater the proportion of the latter, the more rapid is the decomposition, and the greater is the proportion of the chlorate decomposed; but there is no relation between these proportions and the equivalents of the substances employed. The mixtures in equal parts do not undergo any fusion at the temperature of boiling mercury, and only imperfectly when heated on a sand-bath. The phenomenon of incandescence is never produced when the maximum temperature is  $360^{\circ}$ , but is developed with great facility (the mixture in equal parts excepted), when a dull red heat is attained.

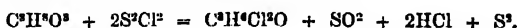
*Influence of Temperature*.—The decomposition of the mixtures generally commences at about  $210^{\circ}$ , or towards  $300^{\circ}$  when the active substance is present in very small proportion. Even at these low temperatures the mixture may be completely decomposed, but the evolution of oxygen is very slow, and the mixture does not enter into fusion. Oxygen so prepared is perfectly free from chlorine. When the temperature is raised to  $310^{\circ}$ – $320^{\circ}$ , gas is evolved violently, there is an emission of heat without ignition, and the temperature passes all at once beyond  $360^{\circ}$ ; at the same time chlorine is liberated, and the mass undergoes complete liquefaction. At a still higher temperature the evolution of gas is still more rapid, and, in fact, the rapidity of the decomposition is in proportion to the temperature.

*Chemical Actions which certain substances exercise upon Potassium Chlorate*.—Potassium chlorate causes the inflammation of sulphur, wood-charcoal, graphite, sulphide of antimony, &c., below the temperature of boiling mercury, and during the reaction there is an enormous development of heat. Substances which react upon this salt generally abstract its oxygen, rarely its chlorine, and sometimes also seize its potash; when the last-named reaction occurs, there is always a large quantity of chlorine produced, due to the decomposition of the chloric acid liberated. When green oxide of chromium is heated in a mercury-bath with this salt, a considerable evolution of chlorine and oxygen occurs even below  $200^{\circ}$ , and the oxide is completely transformed into potassium chromate below  $290^{\circ}$ . Metastannic acid has no action upon the chlorate at  $360^{\circ}$ , but at a higher temperature chlorine and oxygen are evolved, and the residue is strongly alkaline. Tungstic acid begins to act upon the salt at  $270^{\circ}$ , and at  $350^{\circ}$  there is evolution of oxygen with much chlorine, and probably with formation of an alkaline tungstate. Silicic acid acts only beyond the melting point of the chlorate, with evolution of oxygen, chlorine, and excessively pungent white vapours, which may be chloride of silicon. Fused boric acid acts energetically, chlorine being liberated in great abundance.

**CHLORHYDRINS.** *Dichlorhydrin*,  $C^2H^2Cl^2(OH)$ .—According to Hübner a. C. Müller (*Zeitschr. f. Chem.* [2] vi. 344), dichlorhydrin prepared by Bortholot's process (i. 893) boils between  $174^{\circ}$  and  $186^{\circ}$ , and when subjected to fractional distillation does not exhibit any constant boiling point, though larger quantities pass over from  $174^{\circ}$  to  $177^{\circ}$ , and from  $184^{\circ}$  to  $186^{\circ}$ , than at the intermediate temperatures. Both the lower and the higher boiling portions exhibit the composition of dichlorhydrin, whence Hübner a. Müller infer that the dichlorhydrin boiling between  $174^{\circ}$  and  $186^{\circ}$  is a mixture of the two isomerides,  $CH^2Cl-CHCl-CH^2OH$  and  $CH^2Cl-CHOH-CH^2Cl$ .

According to A. Watt, however (*Deut. Chem. Ges. Ber.* v. 257), the portion of the above-mentioned product which boils at  $182^{\circ}$ – $184^{\circ}$  is not homogeneous, but resolvable into two portions of lower and higher boiling point respectively, the latter being very small in quantity. Hence Watt concludes that no second dichlorhydrin is produced, at least in any notable quantity. The same conclusion is arrived at by Markownikoff (*Deut. Chem. Ges. Ber.* vi. 1210), who finds that both the lower and the higher boiling portion yield by oxidation the same product, viz. a crystalline dichloracetone melting at  $43^{\circ}$ .

According to Claus (*Ann. Ch. Pharm.* clx. 42) dichlorhydrin is best prepared by the action of sulphur chloride on anhydrous glycerin:



Glycerin is concentrated till it boils at  $105^{\circ}$ ; 800 grams of it are then placed in a flask connected with a reversed condenser; and 2 kilograms of sulphur chloride are gradually added, the mixture being well shaken and heated in a salt-bath. After seven or eight hours, the condenser is removed, and the product heated for an hour longer to expel sulphur dioxide and hydrogen chloride. The cooled mass is exhausted with ether, the solution first distilled in a water-bath, and the residue distilled over the naked flame. 800 grams of glycerin thus treated yielded 700 grams of pure dichlorhydrin. The by-products consist of sulphuretted bodies of higher boiling point.

Dichlorhydrin has a specific gravity of 1.369 at  $16^{\circ}$ , and boils at  $176^{\circ}$ – $177^{\circ}$  (Watt). By oxidation with *chromic acid* it yields chloracetic acid and dichloracetone (Watt, Claus), and, by further action, hydrochloric acid and carbon dioxide, probably together with formic acid (Claus). By oxidation with *nitric acid* it gives oxalic acid and an oil having the smell of chloropicrin (Watt).

According to Markownikoff (*loc. cit.*) pure dichlorhydrin prepared by addition of hydrochloric acid to epichlorhydrin, is an oily liquid of sp. gr. 1.383 at  $19^{\circ}$ , boiling at  $171^{\circ}$ – $171.5^{\circ}$ , soluble in 19 times its volume of water at  $19^{\circ}$ . By oxidation with chromic acid it is converted into a dichloracetone,  $C^3H^4Cl^2O$ , which crystallises in rhombic plates melting at  $43^{\circ}$ , and is therefore isomeric with the dichloracetone produced by the action of chlorine on acetone, which is a liquid boiling at  $120^{\circ}$ – $121^{\circ}$ . The solid dichloracetone unites with sodium bisulphite, forming the compound  $C^3H^4Cl^2O \cdot SO^2NaH + 3H^2O$ , which crystallises in long four-sided prisms.

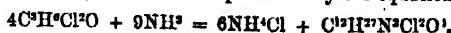
When dichlorhydrin in ethereal solution is added by drops to sodium immersed in anhydrous ether, a violent action takes place, the ether distilling over, and a white saline substance being left which, when separated from the remaining sodium by trituration and sifting, dissolves easily in water. On distilling the aqueous solution till the boiling point rises to  $100^{\circ}$ , and mixing the distillate with potassium carbonate, an oily liquid rises to the surface consisting of allyl alcohol. The action of the sodium is therefore simply to remove the chlorine from the dichlorhydrin:



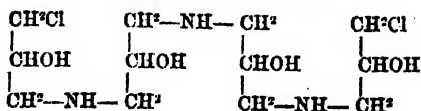
Hydrogen also appears to remove the chlorine from dichlorhydrin without replacement (Hübner a. Müller).

*Action of Ammonia* (Claus, *Ann. Ch. Pharm.* clxviii. 29). Dichlorhydrin heated with alcoholic ammonia yields ammonium chloride and chlorhydrinimide,  $C^3H^3N^2ClO$ . This compound is a white amorphous mass, insoluble in water, alcohol, ether and concentrated acids, not acted upon even by boiling with sulphuric acid, aqua regia, or strong potash-ley. In hot water it swells up enormously and yields a perfectly transparent jelly. It appears to be identical with the compound which Reiboul obtained by the action of alcoholic ammonia on epichlorhydrin. Heated to redness with slaked lime, it yields an oily distillate containing a resin and basic compounds.

The formation of chlorhydrinimide is represented by the equation:



The structural formula assigned to it by Claus is:



8. The formation of chlorhydrinimide in the quantity indicated by the preceding

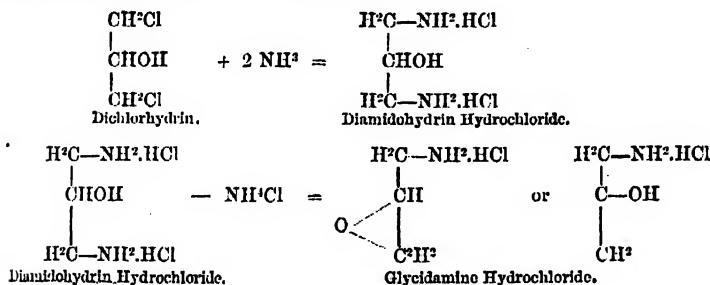
equation takes place only when 9 mol. ammonia are used to 4 mol. dichlorhydrin and the alcohol contains about 4 per cent. of ammonia. When the solution contains only about 1 p. c. ammonia, no chlorhydrinimide is obtained, but the product consists of the hydrochlorides of two new bases, together with sal-ammoniac.

(1). *Diamidohydrin Hydrochloride*,  $C^3H^4N^2O.2HCl$ . This is a very hygroscopic substance, partially decomposed, with formation of ammonium chloride, when the alcoholic solution obtained in the process just described, is filtered from the sal-ammoniac and evaporated. On dissolving it in absolute alcohol and adding platonic chloride, transparent prisms or needles are deposited, having the composition of diamidohydrin platino-chloride,  $C^3H^4N^2O.2HCl.PtCl^4$ .

(2). *Glycidamine Hydrochloride*,  $C^3H^7NO.HCl$ , is obtained in crystals by precipitating the same alcoholic solution with ether: it is also very hygroscopic, but appears to be more stable than the preceding hydrochloride.

The *platinochloride*,  $2(C^3H^7NO.HCl).PtCl^4$ , crystallises in transparent glistening needles. Glycidamine appears to be identical with the glyceramine of Berthelot and De Luca.

The constitution of these bases and the mode of formation of their hydrochlorides may be represented by the following equations:—



**Trichlorhydrin**,  $C^3H^2Cl^3$ . According to Berthelot (*Ann. Ch. Pharm.* clv. 105) the bodies having this composition which are not directly allied to glycerin, are for the most part only isomeric with the true trichlorhydrin obtained from that body (i. 804). To establish the identity of any such compound with trichlorhydrin, he considers it necessary to show that the body in question may be reconverted into glycerin, by substitution of  $3\text{OH}$  for  $3\text{Cl}$ , under the same circumstances as trichlorhydrin itself. It is true that this transformation is difficult, even in the case of the true trichlorhydrin, not being produced by the action of alkalis, or with certainty even by that of moist silver oxide. It may, however, be satisfactorily effected by heating the chloride in a digestion-tube to  $160^\circ$  for 25 to 30 hours with pure water; part of it is then converted into insoluble polyglycerin derivatives, but the greater part into glycerin. Trichlorhydrin is further characterised by boiling at  $155^\circ$ , and by being converted by potash into epidichlorhydrin  $C^3H^4Cl^2$ , boiling at  $101^\circ$ , which in its turn may be transformed into the liquid compound  $C^3H^4Cl$ , boiling at  $164^\circ$ . By these tests, Berthelot has examined the following isomerides of trichlorhydrin:

1.  $C^3H^4Cl^3$  from *Acetone*. Acetone was treated with phosphorus pentachloride, whereby the compound  $C^3H^4Cl^3$  was formed, and this was treated at  $0^\circ$  with dry chlorine. The product separated on distillation into  $C^3H^4Cl^3$  boiling at  $140^\circ$ - $145^\circ$ , and  $C^3H^4Cl^3$  boiling at  $161^\circ$ - $166^\circ$ . Neither of these compounds yielded glycerin when heated with water; and the same negative result was obtained with the compound  $C^3H^4Cl^3Br^2$  produced by direct combination of  $C^3H^4Cl^3$  with bromine. That the above-mentioned acetone derivatives are merely isomeric with those obtained from propylene chloride is seen from their boiling points:

	$C^3H^4Cl^3$	$C^3H^4Cl^3$	$C^3H^4Cl^3$
The propylene compounds boil at	$104^\circ$	$170^\circ$	$195^\circ$ - $200^\circ$
The corresponding acetone derivatives boil at	$70^\circ$	$140^\circ$	$165^\circ$

2.  $C^3H^4Cl^3$  from *Isopropyl Iodide*. This iodide was first converted by the action of chlorine on the corresponding chloride  $C^3H^4Cl$ , and the latter was further chlorinated. Two compounds were thus obtained, namely  $C^3H^4Cl^3$  boiling at  $150^\circ$ - $160^\circ$ , and a camphoroidal body  $C^3H^4Cl^3$  of sp. gr. about 1.55, melting at  $145^\circ$  and boiling at  $180^\circ$ - $190^\circ$ .

The former when heated with water did not yield a trace of glycerin.

3.  $C^3H^5Cl^3$  from Propane. This hydrocarbon, prepared by heating ethyl cyanide with hydriodic acid to  $180^\circ$  was chlorinated by Schorlemmer's method (1st Suppl. 958), whereby two chlorides were obtained, namely  $C^3H^5Cl^2$ , boiling at  $200^\circ$ , and  $C^3H^5Cl^3$ , boiling at  $150^\circ-160^\circ$ . The former was further chlorinated and the product, together with the trichloride just mentioned, was submitted to the action of water. The results were doubtful, as only small quantities of material were employed.

From these facts Berthelot concludes that there are at least five series of isomeric compounds  $C^3H^5X$  (where  $X = Cl, H$ ), namely, those derived: 1. from Propane; 2. from Propylene hydrochloride or Isopropyl chloride; 3. from Normal propylene chloride; 4. from the Acetone derivative  $C^3H^5Cl^2$ ; 5. from Trichlorhydrin; to which perhaps may be annexed as special series, the corresponding derivatives of Allyl chloride, the two Hydrochlorides of Acrolein, the two Hydrochlorides of Allylene, &c.

On the physiological action of trichlorhydrin, see Romansky (*Pflüger's Archiv. für Physiologie*, v. 365: *Chem. Soc. J. x.* 902).

**Epichlorhydrin**,  $C^3H^5ClO$ . This compound unites with sulphuric acid, with great evolution of heat, and forms a thick oil,  $C^3H^5ClO \cdot SO^2H^2$  or  $CH^2OH \cdot CH(SO^2H) \cdot CH_2OH$ , from which the sulphuric acid may be removed by potash (Oppenheim, *Deut. Chem. Ges. Ber.* iii. 735).

**Chlorobromhydrin**,  $C^3H^5(HO)BrCl$ , is prepared by the action of fuming hydrobromic acid on epichlorhydrin. When oxidised by chromic acid, it yields a product which boils at  $176^\circ-188^\circ$ , and solidifies in ice-cold water. On expressing the water from this product, and recrystallising it from ether free from alcohol, crystals of chlorobromacetone  $C^3H^5BrClO$  are obtained, which melt at  $31^\circ-35.5^\circ$ , have a very pungent odour, dissolve easily in alcohol and ether, sparingly in water, and unite with sodium bisulphite (Tegarten, *Deut. Chem. Ges. Ber.* vi. 1212).

**Chloriodhydrins**.—*Dichloriodhydrin*,  $C^3H^5Cl^2I$ , obtained by acting on chloriodhydrin with phosphorus pentachloride, is a colourless liquid, with a faint ethereal smell, boiling at  $205^\circ$ . It is neutral, but soon becomes acid in the moist state (L. Henry, *Deut. Chem. Ges. Ber.* iv. 701).

*Chlorobromiodhydrin*,  $C^3H^5ClBrI$ , obtained by acting with phosphorus pentabromide on chloriodhydrin, is a substance with similar properties, but decomposed on boiling, free iodine and acid vapours being given off (Henry).

**Chloronitrins** (L. Henry, *Ann. Ch. Pharm.* clv. 164). The mono- and di-halogen-hydrins, as well as the epi-halogen-hydrins of glycerin, are acted on by pure hydrogen nitrate,  $HNO^3$ , in such a manner that the OH and O contained in them are replaced by equivalent quantities of the nitric acid residue  $NO^2$ , provided that the only halogens present are chlorine and bromine; with the chloriodo- and bromiodohydrins, the reaction takes place somewhat differently, the iodine as well as the hydroxyl being then replaced by  $NO^2$ . The method of preparing the nitro-halogen-hydrins, is essentially the same as that employed for the preparation of nitroglycerin.

To prepare mono- and di-nitrochlorhydrins, monochlorhydrin, or dichlorhydrin is gradually added to a cooled mixture of equal volumes of fuming nitric and strong sulphuric acid, with vigorous stirring in order to bring the two liquids (which do not mix perfectly) into intimate contact. The reaction takes place very quietly, especially in the case of the dichlorhydrin. When it is complete, the whole is poured into cold water, and the heavy oil produced is washed with solution of sodium carbonate and dehydrated with calcium chloride.

The product consists of monochlorodinitrin  $C^3H^5Cl(NO^2)^2$ , or dichloromononitrin  $C^3H^5Cl^2NO^2$ . The former of these compounds may also be prepared from epichlorhydrin  $C^3H^5ClO$ , by adding the latter very carefully, so as to avoid even local heating, to fuming nitric acid cooled with ice, and pouring the mixture into cold water, whereupon the chloronitrin separates as an oil. To ensure complete conversion, the product is treated with a mixture of nitric and sulphuric acids, and the process is completed in the manner above described when mono- or dichlorhydrin is used as the starting point. The reaction is supposed to consist, first, in the addition of the elements of nitric acid to the epichlorhydrin, forming the compound  $C^3H^5Cl.OH.NO^2$ , and, secondly, in the replacement of the water-residue OH by  $NO^2$ .

*Dichloromononitrin*,  $C^3H^5Cl^2NO^2$ , is a colourless oil having a faintly pungent nitrous odour and a saccharine taste, slightly soluble in water, easily in alcohol and ether, and having a specific gravity of 1.465 at  $10^\circ$ . It distils, with partial decomposition at  $180^\circ-190^\circ$ , therefore, like other nitric ethers, at a temperature differing but slightly from the boiling point of the corresponding alcohol (dichlorhydrin). Heated on platinum foil, it burns quickly with a white flame. Aqueous potash does not act



upon it, but *alcoholic potash* attacks it, even in the cold, forming potassium nitrate, potassium chloride and epichlorhydrin, and finally reducing it to glycerin. From aqueous *hydriodic acid* it eliminates iodine. *Ammonium sulphhydrate* in alcoholic solution reduces it quickly, forming an oil which appears to be the thio-compound  $C^2H^2.Cl^2.SH$ , analogous to dichlorhydrin.

*Monochlorodinitrin*,  $C^2H^2.Cl(NO^2)^2$ , is very much like the preceding compound; it has a specific gravity of 1.5112 at  $0^\circ$ , and appears to be non-volatile. Neither of these chloronitrins can be exploded by pressure or percussion.

In the series of the chloronitrins, the specific gravity increases with the proportion of  $NO^2$ , thus:—

Hydrin containing	$Cl^2$	$Cl^2(NO^2)$	$Cl(NO^2)^2$	$(NO^2)^2$
Sp. gr.	1.347–1.417	1.465	1.5112	1.595–1.606.

*Chlorobromonitrin*,  $C^2H^2.Cl.Br.(NO^2)$ , formed by adding chlorobromhydrin in small quantities to a mixture of nitric and sulphuric acids, is a thick colourless liquid, having a pungent odour and a bitter taste.

**CHLORINE.** *Preparation.*—Deacon's process for preparing chlorine by passing a mixture of hydrogen chloride and oxygen over cupric sulphate or other copper salt heated to  $700^\circ$ – $750^\circ$  F. (1st Suppl. 436), has been explained by its author in a lecture delivered before the Chemical Society on June 20, 1872 (see *Chem. Soc. J.* [2] x. 725–759); abstr. *Chem. News*, xxv. 307). The paper contains an account of numerous experiments both on the laboratory and on the manufacturing scale, the chief results of which are as follow:—

1. The heated mixture of hydrochloric acid gas and oxygen or air does not yield chlorine, except in presence of some substance capable of being attacked by the hydrochloric acid, amongst which the copper-compounds are eminently active. For economic reasons, the sulphate is the salt mostly employed.

2. With the same mixture of gases at the same temperature, the amount of hydrochloric acid decomposed by the aid of a molecule of the copper salt in a given time, depends upon the number of times the molecules of the mixed gases are passed through the sphere of action of the copper salt.

3. There is a certain small range of temperature between the limits of which the percentage of hydrochloric acid decomposed varies greatly; this percentage is higher for the sulphate of copper than for the chloride, but is the same whether solid cupric sulphate is used, or merely pieces of brick saturated with it: hence the amount of action appears to depend upon the surface rather than the mass of the copper salt present.

In experiments on the large scale, the critical temperature is always lower than in laboratory experiments, usually  $100^\circ$  or  $150^\circ$ ; and when the mixed gases are passed through a series of parallel tubes coated internally with cupric sulphate, an increased velocity in the flow of gas yields only about one-third the increase in the amount of chlorine produced, that an irregular porous surface does under the same circumstances.

4. Other conditions remaining the same, the percentage of hydrochloric acid decomposed varies with the square root of the proportionate volume of oxygen to hydrochloric acid.

5. The cupric chloride formed bears no definite proportion to the amount of chlorine produced.

De Lalande a. Frudhomme (*Bull. Soc. Chim.* [2] xvii. 290) find that when a mixture of silica with the chloride of an alkali-metal, alkaline earth-metal, or earth-metal is heated to redness and subjected to the action of a current of air or oxygen gas, chlorine is evolved and the chloride is converted into a silicate: e.g.



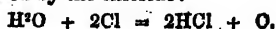
When hydrochloric acid gas is passed, together with oxygen, over the mixture of silica and chloride, the hydrochloric acid reproduces the metallic chloride at each instant by decomposing the silicate:



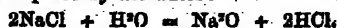
In this manner a continuous evolution of chlorine is obtained.

The water-vapour formed in the preceding reaction gives rise to two secondary reactions:

1. The water is decomposed by the chlorine:



2. The chloride is decomposed by the water:



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Boric, stannic, and phosphoric acids, alumina, pumice-stone, fragments of brick, &c., cause the evolution of chlorine quite as well as silica.

The temperature of the reaction is higher than in Deacon's process, but the quantity of chlorine evolved is the same.

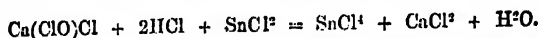
*On the action of Light on Chlorine, and on the Absorption of Light by Chlorine and its Compounds, see LIGHT.*

*Detection and Estimation.*—For Beilstein's method of detecting chlorine, bromine, and iodine in organic substances by heating them with cupric oxide in a gas-flame, see BROMINE (p. 210).

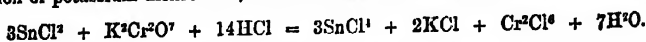
In estimating these elements in organic bodies by Carius's method, it is found that bulbs of ordinary glass are not available, since they lose considerably in weight when heated to 160°–220° with nitric acid of sp. gr. 1.2. Bulbs of Bohemian glass, on the contrary, are scarcely altered.

*Estimation in Bleaching Powder.*—G. E. Davis (*Chem. News*, xxvi. 25) takes advantage of the comparatively easy solubility of arsenious acid in glycerin, to prepare a solution of arsenious acid for chlorometric purposes. He states that it possesses all the advantages and none of the disadvantages of the solution prepared according to Penot's method (4.44 grams of arsenious oxide and 13 grams of crystallised sodium carbonate dissolved in a litre of water). The standard solution is thus prepared: 13.95 grams of powdered arsenious oxide are dissolved by the aid of heat in 40 c.c. of glycerin, and the solution is diluted to one litre. Every 10 c.c. corresponds to 0.1 gram of chlorine. A drop of solution of indigo sulphate is used as an indicator, and the bleaching liquor is run into the arsenic solution until the blue colour of the indigo is destroyed or changed to a brownish yellow. The results obtained by this method are found to agree with those obtained by the use of a solution of arsenious oxide in acid or alkali, and with those of Bunsen's iodometric method.

J. B. Herreshoff (*Chem. News*, xxiii. 29) has given a method for the determination of available chlorine in bleaching powder based upon the fact that when bleaching powder is made to act upon an excess of stannous chloride in strongly acid solutions, stannic chloride is formed at the expense of all the available chlorine of the bleaching powder:



The amount of stannous chloride is afterwards estimated by means of a standard solution of potassium dichromate, and deducted from the amount originally employed:



1 gram of bleaching powder triturated with water is added to 20 cub. cent. of a titrated solution of stannous chloride (30 grams  $\text{SnCl}_2$  dissolved in water with addition of hydrochloric acid, and diluted to 1000 c.c.) and afterwards 10 or 12 c.c. of hydrochloric acid. The reaction is energetic and complete, and yields a perfectly colourless solution. This liquid is then treated with a few drops of starch-paste and potassium iodide, and the excess of stannous chloride is determined with potassium dichromate (13.8738 grams in 1000 c.c.) added till a permanent blue colour is produced.

G. Lunge (*Chem. News*, xxiv. 5) regards this method as unsatisfactory, on the ground that the strength of the tin-solution is very variable. He gives the preference to Mohr's method of estimation with arsenious acid (i. 904), and replies to certain objections urged by Herreshoff against it, namely, that it is difficult to ascertain the purity of the arsenious acid employed; that the dissolution of this acid in sodium carbonate takes a long time; and that the solution thus formed does not remain of constant strength. Lunge, on the other hand, finds that the purity of any sample of arsenious acid is easily tested by sublimation; if pure, it will sublime completely and yield a perfectly white sublimate (sulphides of arsenic, if present, would give the sublimate a reddish tinge); further that the arsenious acid dissolves very quickly in aqueous sodium carbonate, if the proportions recommended by Mohr and by Fresenius are followed; and lastly, that a solution of pure arsenious acid will preserve its strength unaltered for years. Lunge titrates it with iodine, and recommends that the arsenious acid be poured into the iodine-solution.

A. H. Massey (*Chem. News*, xxiv. 271) examined three samples of bleaching powder by Herreshoff's method and by the arsenic method, and found that in each case the two methods gave concordant results.

According to J. Smyth (*ibid.* 75) the milky solution of chloride of lime is but so well adapted for chlorimetry as a clear solution obtained by dissolving the bleaching powder in an alkaline liquid. 10 grams of chloride of lime are added to a solution of 20 grams of sodium carbonate; the liquid is filtered from the precipitated calcium carbonate; the precipitate washed till the wash-water no longer bleaches indigo; and

the liquid is diluted to a litre. The resulting solution is well adapted for chlorimetry, and presents the further advantage of an easy estimation of the lime by precipitation with a titrated solution of sodium carbonate.

In the method of chlorimetry depending on the oxidation of ferrous sulphate by a hypochlorite (i. 904), it has been proposed to substitute ammonio-ferrous sulphate for the simple ferrous sulphate, inasmuch as it is more easily obtained and kept in a perfectly definite state. According to E. Biltz, however (*Arch. Pharm.* [2] cxlvi. 97), the double salt does not give exact results, because the chlorine acts on the ammonia as well as on the ferrous salt, as is shown by the evolution of gas which takes place on adding the ammonia salt to chlorine water. The error thence ensuing, which in the most favourable case entails a loss of  $\frac{1}{2}$  p. c. of the chlorine present, is not constant, but varies considerably according to the quantity of water added to the solution of the double salt.

**CHLORITE.** From a discussion of the published analyses of the several varieties of chlorite, including pennine and clinocllore, Konngott (*Jahrb. pr. Chem.* ci. 17) infers that they may all be included under the general formula  $RO.H^2O + 2(RO.SiO^2)$ , assuming that the group  $RO.SiO^2$  may be more or less replaced by  $Al^2O^3$ .

A mineral called diabantachronny, which gives the colour to the green diabases of the Vorgtland and the Frankenwald, was examined by K. Liebe (*Jahrb. f. Mineralogie*, 1870, i.; *Jahrb.* 1870, 1307), and regarded by him as a distinct species. Konngott, however (*Jahrbuch f. Mineralogie*, 1871, 51) has shown from Liebe's analyses, that it is a variety of chlorite. Seven analyses of carefully selected specimens of diabantachronny gave the following results:—

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	MgO	FeO	H <sup>2</sup> O
I. . . . .	30.27	11.16	—	21.22	26.94	10.20
II. . . . .	29.37	12.00	—	21.01	25.63	11.27
III. . . . .	29.85	9.07	—	17.92	26.60	15.81
IV. . . . .	31.25	10.03	3.47	19.73	23.52	11.37
V. . . . .	31.69	12.22	—	22.05	21.26	12.17
VI. . . . .	31.38	11.89	—	22.91	22.72	10.91
VII. . . . .	31.56	12.08	—	22.44	21.61	11.78

These numbers yield the following ratios:—

	I.	II.	III.	IV.	V.	VI.	VII.
Silica . . . . .	5.05	4.89	4.97	5.21	5.28	5.23	5.26
Alumina . . . . .	1.08	1.16	0.88	0.97	1.19	1.15	1.17
Ferric oxide . . . . .	—	—	—	0.22	—	—	—
Magnesia . . . . .	5.30	5.25	4.48	4.93	5.51	5.73	5.61
Ferrous oxide . . . . .	3.74	3.56	3.60	3.27	2.95	3.16	3.00
Water . . . . .	5.67	6.26	8.78	6.32	6.93	6.06	6.54

If now we resolve the alumina into  $AlO^2$  and  $AlO$ , and add these to the  $SiO^2$  and  $RO$  respectively, the same being done in IV. with the ferric oxide, we have—

	I.	II.	III.	IV.	V.	VI.	VII.
SiO <sup>2</sup> + AlO <sup>2</sup> . . . . .	6.13	6.05	5.85	6.40	6.47	6.3	6.43
RO + AlO . . . . .	10.12	9.97	9.05	9.39	9.65	10.0	9.78
2H <sup>2</sup> O . . . . .	2.83	3.13	4.39	3.16	3.46	3.03	3.26
Or,							
SiO <sup>2</sup> + AlO <sup>3</sup> . . . . .	2.00	2.00	2.00	2.00	2.00	2.00	2.00
RO + AlO . . . . .	3.30	3.30	3.09	2.93	2.98	3.16	3.04
2H <sup>2</sup> O . . . . .	0.92	1.03	1.50	0.97	1.07	0.95	1.01

These proportions agree for the most part with the chlorite formula. The disparity in III. of 1.50 instead of 1(2H<sup>2</sup>O) doubtless arises from an error in analysis, the exact estimation of the water presenting considerable difficulty.

**CHLOROCODIDE.** See CODEINE.

**CHLOROFORM, CHCl<sup>3</sup>.**—This compound is formed by the action of phosphorus pentachloride on iodoform:



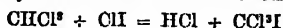
There is also formed a very small quantity of a liquid containing a large proportion of iodine, and decomposing quickly, with rise of temperature, on exposure to the air (Gautier, *Bull. Soc. Chim.* [2] xiii. 127). The action of phosphorus pentachloride on iodoform was first studied by Serullas, who obtained an iodised product, regarded by Butlerow as methylene iodide (CH<sup>2</sup>I<sup>2</sup>) (iii. 311, 1006).

According to Bolohoubek (*Ann. Ch. Pharm.* clxv. 240), pure methyl alcohol, obtained from the crystalline oxalate, does not yield chloroform when treated with bleaching powder and water. Neither is chloroform obtained by treating acetic acid with aqueous bleaching powder. Now Lieben has shown that pure methyl alcohol and acetic acid yield no iodoform, although ethyl alcohol, aldehyde, and acetone do yield that compound under the influence of certain reagents. Probably, therefore, bodies which do not yield iodoform are likewise incapable of producing chloroform. The formation of chloroform by heating dry acetates with bleaching powder, is probably due to the acetone formed in the first instance.

Chloroform heated with bromine to 200° for six or eight hours yields a product from which, by fractional distillation, bromotrichloromethane CBrCl<sup>3</sup> is obtained, together with a small quantity of a liquid of higher boiling point, probably CBr<sup>2</sup>CCl<sup>2</sup> (Paternò, *Gazzetta chimica italiana*, i. 593.—Friedel a. Silva *Bull. Soc. Chim.* [2] xvii. 537). The compound CBrCl<sup>3</sup> is a mobile colourless liquid becoming coloured on exposure to light. It has a pleasant ethereal odour, dissolves in alcohol and ether, boils at 104.3° under a pressure of 757.9 m.m. (Paternò); at 103°–104° under a pressure of 752 m.m. (F. and S.) Its specific gravity is 2.063 at 0°, 2.016 at 25°. When it is mixed with ether and acted upon by sodium, its chlorine and bromine are slowly attacked; sodium alone does not act upon it even when heated, but potassium produces a violent explosion (F. and S.).

Chloroform heated to 150° for three hours with 3 parts bromine and 1 part iodine in sealed tubes, which are opened occasionally to allow escape of gas, yields a liquid from which by fractional distillation are obtained tribromochloromethane CBr<sup>3</sup>Cl, melting at 70° and tetrachloromethane or carbon tetrachloride, melting at 76° (Bolas a. Groves, *Chem. Soc. J.* [2] ix. 779).

In like manner when chloroform is heated to 160°–170° in a sealed tube with iodine monochloride, tetrachloromethane is obtained, together with a small quantity of trichloro-iodomethane, the latter being doubtless the first product, and being converted into the former by the further action of the iodine monochloride:



and



(Friedel a. Silva, *loc. cit.*)

Chloroform may be converted into chloropierin, C(NO<sup>2</sup>)Cl<sup>3</sup>, by heating 7 vol. of it with 16 vol. hydrogen nitrate (HNO<sup>3</sup>), containing much nitrogen tetroxide, in sealed tubes to 90°–100° for 120 hours. The digesting tubes should be at an angle of about 30° with the bottom of the bath, as a more nearly horizontal position is found to involve the destruction of any nitro-compound that may be formed, while an upright position causes the reaction to proceed very slowly. When the digestion is ended, the apparent volume of the chloroform is much greater than before, on account of the liquefied gases, especially nitrogen tetroxide, which it now holds in solution. The tubes are best opened by means of a flame, and allowed to stand about 12 hours; their contents are then poured into water (with which they are washed), and are afterwards dried over calcium chloride and fractionally distilled.

In the course of the distillation, much chloroform comes over first, and is followed by a very small quantity of chloropierin.

Pure nitric acid not containing nitrogen tetroxide attacks chloroform with much greater difficulty and it is very doubtful whether any chloropierin is formed. This observation, taken in connection with the fact that chloroform dissolves nitrogen tetroxide much more readily than nitric acid does, raises a fair presumption that the tetroxide is the actual agent of nitration (E. J. Mills, *Chem. Soc. J.* [2] ix. 443).

**Detection of Chloroform.**—To detect small quantities of chloroform, especially in

presence of etheral compounds closely allied to it, and possessing similar properties, advantage may be taken of its behaviour with the *monamines* in presence of alcohol and sodium hydrate. The odour of isonitrils thereby produced is an infallible sign of the presence of chloroform. The experiment is performed by adding the liquid to be tested to a mixture of aniline—any other primary monamino, fatty or aromatic, serves equally well—and alcoholic soda. If chloroform is present, a violent reaction takes place, either immediately or on warming gently, and the peculiar-smelling vapour of the isonitril is evolved. Bromoform and iodoform, of course, behave like chloroform: the reaction occurs, moreover, with all bodies capable of yielding chloroform, bromoform, or iodoform by the action of alkalis. For example, on adding a solution of chloral in aniline to alcoholic potash, the vapour of an isonitril is immediately evolved in abundance. *Chlorethylidene* treated with alcoholic potash and aniline, yields no isonitril, and is therefore easily distinguished from chloroform. The reaction here recommended is so delicate, that one part of chloroform dissolved in 5,000 to 6,000 parts of alcohol may be detected by it with certainty (A. W. Hofmann, *Deut. Chem. Ges. Ber.* iii. 769).

On the detection of alcohol in chloroform, see ETHYL ALCOHOL.

**CHLOROPHYLL. Absorption-spectrum.**—In the spectrum of light transmitted through a concentrated solution of chlorophyll, all the light is absorbed, except the least refrangible red, near the line B. On gradually diluting the solution, the green first makes its appearance, then the yellow, the orange, and part of the red, forming a very characteristic spectrum containing—I, a broad dark band close behind B, which is darkest between B and C; II, a second absorption-band in the orange between C and D; III, a third a little behind D; and a fourth, IV, in the green close before F. Of these bands, I, is by far the darkest, making its appearance even in very dilute solutions, whilst II, III, and IV, gradually diminish in intensity. The whole of the more refrangible portion of the spectrum is also absorbed, but just before G the absorption is somewhat weaker, increasing again behind G; and in the green behind  $\delta$ , is a band V, which does not appear in fresh solutions of leaf-green, but only in those which have been modified by the action of light.

When a solution of chlorophyll is illuminated by a pure sun-spectrum, the red fluorescent light is seen over all the spectrum with the exception of the extreme red, beginning just before B, and extending with varying intensity to the ultra-violet. In this spectrum seven bright bands may be observed: the first between B and C; the second between C and D, rather nearer to D; the third close behind D; the fourth immediately before E; the fifth, which is seen only in the modified solution, behind  $\delta$ ; and the sixth and seventh, beginning behind F, cover the rest of the spectrum. Of these, the first, between B and C, and the sixth and seventh are the brightest. These bright fluorescent bands correspond both in position and intensity with the dark absorption-bands, showing the intimate relation between fluorescence and absorption. The red fluorescent light, when concentrated and examined spectrally, is found to consist entirely of red rays corresponding in refrangibility with those between B and C.

The absorption-spectrum of solid chlorophyll has a great resemblance to that of the solution, a thick layer of green leaves absorbing all the rays of the spectrum from B to the violet end. A thinner layer shows a dark band beginning before B and reaching to behind C; it transmits the red, orange, yellow, and green light between C and E; just behind E the spectrum begins to darken, and from the middle point between F and G it is opaque. The dark bands II, III, and IV, of the solution do not appear, powerful absorption only being found in the violet, and in the red between B and C. As solid chlorophyll does not exhibit the phenomenon of fluorescence, the red rays between B and C can only be indirectly absorbed (Lommel, *Pogg. Ann.* cxl. iii. 568).

**Modification of Chlorophyll by Light. a.**—It has long been known that a chlorophyll solution when exposed to light becomes changed in colour, and Stokes (*Pogg. Ann. Erg.* iv. 128) has found that this chlorophyll, precipitated from its alcoholic solution and again dissolved in ether, undergoes no further change when exposed to diffused light. This *modified* chlorophyll has a somewhat different spectrum from the fresh, the dark band III, being lighter and displaced towards the more refrangible end of the spectrum, whilst there is a bright band between  $\delta$  and F, so that, in the modified chlorophyll, there are five dark bands between a and F, whilst in the fresh there are only four. In order to investigate this change more thoroughly, Gerland (*Pogg. Ann.* cxliii, 585) has examined the absorption-spectra of various chlorophyll solutions, both prior to exposure, and at intervals during insolation.

1. **Alcoholic Solution of fresh Chlorophyll.**—This solution, which was simply an alcoholic extract of the leaves of *Urtica dioica*, previously boiled in water, showed the band III, very distinctly and stronger than IV, which was very feeble. Exposed to

sunlight it had perceptibly changed colour in five minutes, in ten it was olive green, in fifteen brown, and after the lapse of an hour it had become bright yellow, and no longer showed any signs of fluorescence. During this change the absorption-bands gradually became more indistinct, and disappeared in their order, I. being the most stable; eight days' insolation rendered it almost colourless in thin layers, but in thicker layers it appeared of a brownish yellow, and gave the same absorption-spectrum as Fülho's yellow (*Ann. Chim. Phys.* [4] xiv.). The same change took place in diffused light, but more slowly. The alcoholic solution of the leaves of *Urtica dioica* which had been previously treated with cold water, as also that prepared from *Sambucus nigra*, which had been boiled with water, gave the same spectrum, although the solutions differed slightly in colour.

2. *Alcoholic Solution of half-modified Chlorophyll.*—A solution which had been prepared from the leaves of *Brassica oleracea* in December 1870, and exposed to a diffused light for about two months, gave a spectrum between that of fresh and that of modified chlorophyll. Its colour was brownish-green, and gave the dark band III. but weakly, whilst V. was scarcely distinguishable. Exposed to insolation, it gradually faded, but more slowly than the freshly prepared solution; for even after being exposed to sunshine for eight hours, and to daylight during several days, it still showed all the dark bands except III., but much more faintly than before. After another eight hours' sunshine and several days more of diffused light, I. was still very faintly visible, and even when it was submitted to insolation for six hours more, a considerable thickness of the solution showed traces of the band I. A solution, prepared in 1863, and kept in the dark for 3½ years, gave the same results.

3. *Completely modified Chlorophyll.*—An ethereal solution of modified chlorophyll becomes faded, but very slowly; after 42 hours' insolation, a stratum of the solution 15 m.m. thick had the same colour as one of the original solution 2.5 m.m. thick, but all the bands were visible, and even after forty days' exposure to light, I. was still faintly visible, and the solution distinctly fluorescent. An alcoholic solution behaved in the same way, but the change took place much more rapidly.

4. *Ethereal Solution of Fresh Chlorophyll.*—This was obtained from *Urtica dioica* in a similar manner to the alcoholic solution, and had the same spectrum, but the bands, with the exception of I. being darker, rendered it more characteristic. Exposed to the sun's rays, it faded much more slowly than the corresponding alcoholic solution, being only slightly changed. After one and a-half hour's action, and although it now showed the bright band of modified chlorophyll, the dark band III. was not displaced. The latter, however, was much broader, so that it occupied the space covered by the dark bands both in modified and in fresh chlorophyll. On continuing the insolation, a more rapid change took place, the colour became browner, and after a time III. disappeared, giving the spectrum of the incompletely modified chlorophyll.

5. *Solid Chlorophyll*, precipitated on paper from its alcoholic or ethereal solution, fades completely and rapidly in sunlight, but more slowly in diffused daylight. The chlorophyll cells in a leaf of *Sambucus nigra*, from which the epidermis had been removed, became colourless on exposure to sunlight.

6. *Ethereal Solution of Frémy's Phylloxanthin* (1st Suppl. 443), when submitted to insolation, behaved precisely like modified chlorophyll.

7. *Alcoholic Solution of Fülho's Green* (*Ann. Chim. Phys.* [4] xiv.) became completely faded by long-continued insolation, showing no trace of absorption or fluorescence. When the solution is evaporated, it leaves a colourless waxy substance which froths with sulphuric acid, but not with hydrochloric acid or nitric acid. This green behaves in the same manner whether prepared from dried or from fresh leaves.

As the chlorophyll in plants is evolved from a yellow colouring substance, so does it again become yellow on fading, and therefore it is possible that the yellow residue which is left in autumn leaves, may be faded chlorophyll.

8.—Hitherto no distinction has been made between modified and faded chlorophyll, so that the theories respecting its fading and decolorisation are very contradictory.

Jodin (*Compt. rend.* lix. 859) found that an alcoholic solution of chlorophyll exposed to sunlight absorbed oxygen, whilst Timiriaseff (*Botan. Zeit.*, xxvii. 886), states the fading to be a process of reduction. The latter view appears to be borne out by the observation made by Rauwenhoff and Gerland, that in one instance there was an odour of aldehyde in the alcoholic solution from which modified chlorophyll had been precipitated. Gerland has since frequently repeated this experiment, but has not again been able to detect aldehyde, and has therefore endeavoured to settle this point by insulating two exactly similar test-tubes of chlorophyll solution through one of which oxygen or ozonified air was passed, but it faded with nearly equal rapidity in both cases.

As neither the ether nor the alcohol employed as solvent undergoes any change when the chlorophyll fades, if the fading is due to oxidation, the oxygen must be taken from the air or from that dissolved in the alcohol. When strongly ozonified air was passed into a boiled alcoholic solution of chlorophyll standing over mercury, a small quantity of gas was at first absorbed, and the solution became somewhat darker, but after that no further absorption took place. The presence of oxygen is necessary, however, to start the action, for both the alcoholic and ethereal solutions which had been sealed up in glass tubes from which the air had been expelled by boiling the liquid, could be exposed to the sun's rays without undergoing any change, but directly the air was admitted and they were submitted to insolation, the colour of the solutions began to fade. It would seem, therefore, that both oxygen and light are necessary to produce chemical change in chlorophyll, so that when the solution is exposed to light and air, oxygen first combines with the chlorophyll which begins to be modified, and then, if the insolation be continued, it fades, but if it is exposed only to a feeble light, the oxidation at first set up continues and the chlorophyll becomes modified.

III.—As the dark bands disappear when chlorophyll fades and becomes decolorised, it seems probable that the rays absorbed by the solution are employed in producing chemical action. To test the accuracy of this view, a chlorophyll solution was first submitted to the action of the rays of different parts of the spectrum, but no satisfactory result was obtained. Sach (*Handbuch Exper. Phys. Pflanz.*) had observed that when a chlorophyll solution is exposed to light which has previously passed through another stratum of the same fluid, it does not begin to fade until the other is much changed. Gerland, on repeating the experiment, found that when the protected or test solution began to fade, the band I. in the spectrum of the protecting solution had become foggy and indistinct, whilst the dark bands II. and III. had completely vanished. As therefore light of a refrangibility corresponding with the dark bands II., III., IV. and V. had produced no effect upon the test-solution, it could only be the rays of the same refrangibility as I., and the blue, that caused the solution to fade. When the protecting solution was a concentrated ethereal solution of modified chlorophyll, no change took place in the test-solution even after several days' insolation. On examining this protecting solution spectroscopically, the band I. was seen to be quite black, whilst the red and yellow rays on each side of it were freely transmitted. From the results of this series of experiments, it seemed that the obscure heat-rays took no part in causing the chlorophyll to fade, and in order to confirm this, a solution of chlorophyll was exposed to bright sunshine from which the heat-rays had been excluded by passing it through a stratum of water 130 mm. thick. The colour of the solution, however, faded as quickly as that of one exposed to the direct rays of the sun. In order to ascertain whether it was the red rays corresponding with the band I. or the blue and violet from G to II, or both of these, which caused the change, solutions of chlorophyll were exposed behind red glasses (coloured with copper oxide), and an ammoniacal solution of copper sulphate respectively. The colour of the solution slowly faded in both cases; but on exposing the solution to the light transmitted through green glasses (consisting of the green and a few yellow and blue rays) no change took place: hence it is inferred that chlorophyll fades only when exposed to light of the same refrangibility as that which it absorbs.

It has been shown by Filhol that chlorophyll is composed of two substances, one green the other yellow, which may be separated from one another by filtration through animal charcoal or by the action of oxalic or tartaric acid (*1st Suppl.* 444). This result has been confirmed by Gerland & Rauwenhoff (*Pogg. Ann.* cxliii. 231), who find however, in accordance with Schön and other observers, that these two colouring matters are not the phylloxanthin and phyllocyanin described by Frémy; the phylloxanthin of this chemist appears indeed to be nothing but modified chlorophyll. Neither are the substances in question identical with the yellow and green colouring matters which Kromayer obtained by treating chlorophyll with alcoholic potash (*Jahresber.* 1861, 738). Neither these two substances nor those obtained by Frémy are capable of reproducing chlorophyll by their union.

In leaves which become yellow, the chlorophyll disappears either by being absorbed, or by being converted into the yellow compound (Gerland & Rauwenhoff).

J. Chautard (*Compt. rend.* lxxv. 1836) observes that the dark band in the red of the chlorophyll spectrum is very persistent even under great dilution. The spectrum is considerably altered by adding hydrochloric acid to the solution, but the band in the red is still seen even after great dilution. An alcoholic solution prepared from dried leaves gives a spectrum like that of the acidified solution of fresh leaves. The solution of fresh chlorophyll is also rapidly changed by exposure to sunshine, and more slowly by diffused light, so as to give a spectrum like that of acidified chlorophyll. Other colouring matters do not mask the presence of chlorophyll; and metallic salts do not affect its spectrum before precipitation takes place.

An alcoholic solution of chlorophyll mixed with a few drops of solution of caustic potash or ammonia is very little changed. But by boiling with solution of caustic potash, the characteristic absorption-band in the red is divided into two, whilst the rest of the chlorophyll bands disappear almost entirely. These two bands reunite on acidifying the liquid with acetic acid, and may be again separated by adding ammonia, (Chautard, *ibid.* lxxvi. 570).

According to F. A. Hartmann (*Chem. Centr.* 1872, 524), chlorophyll in the leaves of plants is generally accompanied by a yellow crystalline body. This substance, called *chrysophyll*, and perhaps identical with Frémy's *phyloxanthin*, is obtained, (together with chlorophyll) in small crystals, having a gold-yellow colour, by treating the leaves, previously freed from water by means of alcohol, with ethereal alcohol, pouring off the liquid after 24 hours' standing, and allowing it to evaporate spontaneously. The residue while still moist is treated with petroleum or boiling caustic potash, which dissolves only the chlorophyll, and the remaining *chrysophyll* is recrystallised from ether.

The green mass obtained by evaporation of the ethereal extract from leaves, yields, with hydrochloric acid, a greenish solution, from which, on addition of water, a black substance called *melanophyll* is precipitated.

Chlorophyll is carried down from its solution together with many precipitates, as barium sulphate, calcium oxalate, silver chloride, &c.

**CHLOROPICRIN**,  $C(NO^2)Cl^2$ . *Trichloronitromethane*.—This substance may be prepared by direct nitration of chloroform with strong nitric acid (Mills, p. 324). Cossa (*Gazzetta chimica italiana*, ii. 181) follows the same process, with addition of oil of vitriol.

In preparing chloropicrin by the action of calcium hypochlorite on picric acid (Stenhouse's method, i. 223), Cossa recommends that the mixture of picric acid with perfectly fresh and dry calcium hypochlorite, be passed through a sieve to retain any lumps, which often cause explosion. The best temperature for the reaction is  $45^\circ$ . The chloropicrin thus obtained boils at  $112.8^\circ$ , at 743 mm. pressure, and distils without decomposition. When it is suddenly heated at a temperature above its boiling point, and the vapour is passed through a red-hot tube, it decomposes without explosion, as is also the case when sodium or potassium is fused in it. Chloropicrin readily dissolves iodine, the colour of the solution being deeper than that of iodine in chloroform. It also dissolves cinnamic and benzoic acid, resins, and most substances rich in carbon, including that modification of dinitronaphthalene which is difficultly soluble in alcohol. It is miscible in all proportions with benzene, amyl alcohol, carbon sulphide, and absolute alcohol. At  $11^\circ$ , 1 vol. of 80.5 p. c. alcohol dissolves 3.7 vols., and 1 vol. 78 p. c. alcohol 1.3 vol. chloropicrin; 1 vol. ether dissolves only 0.3 vol.

The reaction which takes place when ammonium sulphide is added to chloropicrin, or when hydrogen sulphide is passed into a solution of chloropicrin in ammoniacal alcohol, is very energetic, and affords the best means of detecting small quantities of chloropicrin in very dilute alcoholic solution. The liquid becomes hot, a deep red colour is produced, sulphur is set free, and much ammonium chloride formed.

Chloropicrin has a more violent action on the respiratory mucous membrane than either chlorine or nitrous fumes, causing suffocation and spitting of blood.

**CHOLESTERIN**,  $C^{26}H^{44}O$ . This substance is contained in the grease of sheep's wool. F. Hartmann (*Inaug. Diss.* Göttingen, 1868) by boiling the grease with alcoholic potash and crystallising the unsaponified residue from alcohol, obtained crystals which exhibited the reactions of cholesterol, but differed considerably from it in appearance, melting point, and composition. Hartmann regarded these crystals as a mixture of cholesterol with unaltered cholesteryl ethers. By heating them with potash-solution in a sealed tube, he obtained crystals which appeared to be purer cholesterol and melted at  $137^\circ$ .

These results have been fully confirmed by E. Schulze (*Zeitschr. f. Chem.* [2] vi. 453), who has obtained the cholesterol in the pure state. 120 grams of the wool-grease were boiled for some hours with potash-solution in a porcelain dish, common salt then added, and the boiling continued for half-an-hour longer. After cooling, the semifluid mass of soap and unsaponified fat was separated from the liquid, and freed from unsaponified fat by digestion with ether. This unsaponified fat, amounting to about 70 p. c. of the original grease, was heated with alcoholic potash for 20 hours to  $100^\circ$  in a closed stone-ware bottle; the contents then poured out; the alcohol evaporated; the greater part of the potash dissolved out of the residue by water; and the undissolved substance stirred up with water and agitated in a glass cylinder with ether. The ethereal layer, when left to evaporate, yielded a faintly yellow fatty substance, a very concentrated solution of which in hot ether solidified on cooling to a mass of needles.



shaped crystals, and a solution of the same in hot alcohol deposited on cooling a considerable quantity of crystalline laminae and white flocks.

The substance thus obtained is a mixture of cholesterol with one or two substances containing less carbon and melting at lower temperatures; by fractional crystallisation from ether-alcohol it yields pure cholesterol in thin shining plates, having exactly the appearance and composition of cholesterol from gall-stones, exhibiting similar reactions, and melting at  $144.5^{\circ}$ . On triturating it with a little concentrated sulphuric acid and then adding chloroform, a blood-red solution is formed, which, on addition of strong nitric acid, becomes violet, blue, and afterwards colourless. On triturating it with a drop of a mixture of 3 vol. strong hydrochloric acid and 1 vol. solution of ferric chloride, and slowly evaporating to dryness, the particles which have remained undissolved assume a violet-red colour, changing to blue. A small portion of the crystals treated with a drop of strong nitric acid and slowly evaporated, leaves a yellow spot turned red by ammonia (compare 1st Suppl. 447).

The reaction of cholesterol with sulphuric acid is best exhibited by dissolving a few centigrams of cholesterol in about 2 c. c. of chloroform, and then shaking it with its own bulk of strong sulphuric acid. The chloroform quickly becomes blood-red, and then cherry-red or purple, a colour which it retains for several days. A few drops poured into a basin become blue, green, and then yellow. This change seems to be due to traces of moisture, and the original colour may be restored by sulphuric acid. The sulphuric acid under the chloroform presents a distinct green fluorescence. When dropped into glacial acetic acid, the liquid, in about half an hour, becomes violet, or, if much diluted, rose-coloured, with a green fluorescence, and exhibits such a resemblance to the liquid obtained by diluting Pottenkofer's test for bile-acids with glacial acetic acid, that it is often impossible to distinguish between them. The spectra they present are also very much alike, but the spectrum of each is somewhat variable. That of the cholesterol solution indicates that it consists of two substances, whose proportions vary. Water takes up from the chloroform solution a sulpho-acid, which forms crystallisable salts with barium. The reaction of cholesterol with sulphuric acid is slightly modified when only traces of cholesterol are present, and it is best in that case to dissolve a few granules in 1 c. c. of chloroform, and warm gently with an equal volume of sulphuric acid, occasionally shaking. The chloroform quickly acquires a rose or violet colour. The sulphuric acid becomes lemon-yellow, with a distinct green reflection. By dilution with glacial acetic acid, a liquid is obtained of a faint red colour, with green fluorescence (E. Salkowski, *Pflüger's Archiv f. Physiologie*, vi. 207).

Cholesterol, boiled for twelve hours with sulphuric acid and potassium dichromate, becomes oxidised, yielding a white amorphous acid product having the composition of oxycholic acid  $C^{24}H^{40}O^6$ , together with small quantities of several of the lower terms of the fatty acid series, probably acetic, propionic, and butyric. Oxycholic acid is not affected by sodium-amalgam in alkaline solution, and is but slowly oxidised by fusion with potassium hydrate, yielding only secondary products of decomposition, viz., inflammable gases, a brown fatty substance, and some of the lower fatty acids (L. Henry, *Deut. Chem. Ges. Ber.* v. 569).

Cholesteryl acetate,  $C^{26}H^{42}.C^2H^3O^2$ , is produced by treating cholesterol with acetyl chloride; it crystallises in small colourless needles, melting at  $92^{\circ}$  (Henry); compare 1st Suppl. 448.

Cholesterylamine,  $C^{26}H^{42}.NH^2$ .—The chloride obtained by the action of phosphorus pentachloride on cholesterol is readily converted into this compound by digestion with alcoholic ammonia. It crystallises in small plates melting at  $104^{\circ}$  (Henry).

The following cholesterol derivatives are now known:—

$C^{26}H^{42}.OH$	:	:	:	:	Cholesterolin.
$C^{26}H^{42}.ONa$	:	:	:	:	Sodium cholesterylato.
$C^{26}H^{42}.OC^2H^3O$	:	:	:	:	Acetyl-cholesteryl.
$C^{26}H^{42}.Cl$	:	:	:	:	Cholesteryl chloride.
$C^{26}H^{42}.NH^2$	:	:	:	:	Cholesterylamine.

Cholesterol treated with phosphorus trichloride yields neutral phosphoretted bodies, which are difficult to purify, and resemble the so-called myelin (Grupe-Besanes, *Ann. Ch. Pharm.* clvii. 284).

The substances above mentioned as obtained together with cholesterol, by the saponification of wool-grease, consists chiefly of an isomeride of cholesterol, which separates from alcohol in white flocks. The portion of wool-grease which does not dissolve in alcohol consists of ethers of cholesterol and ischolesterol; the portion soluble in alcohol contains free cholesterol, and probably free ischolesterol, together with fatty ethers of both these alcohols (Schulze). See ISCHOLESTERIN.

**CHOLIC ACID**,  $C^{25}H^{40}O^3$  (Baumstark, *Deut. Chem. Ges. Ber.* v. 1185, 1377).—This acid is diatomic and monobasic, two of its hydrogen-atoms being replaceable by alcohol-radicles, but only one by metals.

**Ethyl cholate**,  $C^{27}H^{50}(C^2H^5)O^3$ , is prepared by passing hydrochloric acid-gas into a solution of cholic acid in ethyl alcohol, precipitating with water, heating the precipitate with solution of sodium carbonate, and dissolving the portion not thereby taken up, in ether. On evaporating the ether, ethyl cholate remains as a soft unctuous mass, which, when placed over sulphuric acid and frequently stirred, dries up to a resin resembling colophony. [Hoppe-Seyler (*J. pr. Chem.* lxxxix. 272) describes both ethyl and methyl cholates as well crystallised compounds.] It is insoluble in water, very soluble in alcohol and in ether. Caustic alkalis in the cold, and alkaline carbonates with the aid of heat, do not extract from it anything precipitable by acids; but when heated with caustic soda to  $120^\circ$  in a tube, it yields sodium cholate and ethyl alcohol.

It has not been found possible to prepare a diethylic cholate by heating the monethylic ether, or the acid itself, with ethyl chloride.

**Ethyl-Benzoyl Cholate**,  $C^{31}H^{50}(C^7H^5O)(C^2H^5)O^3$ , is produced by heating ethyl cholate with benzoyl chloride in a flask with reversed condenser; and may be purified in the same way as the preceding ether, excepting that it must be heated for some time to  $130^\circ$  to remove adhering benzoic acid. It is a resinous mass, insoluble in water, easily soluble in alcohol and in ether, resolved by heating with alkalis into benzoic acid and ethyl alcohol.

**Cholamide**,  $C^{27}H^{50}O^4.NH^2$ , is formed by heating ethyl cholate with alcoholic ammonia to  $120^\circ$  (according to Hoppe-Seyler the product consists of ammonium cholate). Prepared in this way, or by heating ammonium cholate in an oil-bath as long as water continues to escape, it is a yellowish resinous mass, insoluble in water, moderately soluble in acids, easily in alcohol and ether, decomposing at high temperatures.

**Products of Decomposition of Cholic Acid**.—This acid, subjected to gradual oxidation, yields a condensed acid which appears to contain not less than 96 atoms of carbon, and is, perhaps, the acid which has been described as choloic acid.

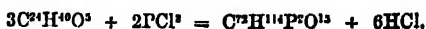
By dry distillation cholic acid yields a small quantity of a substance exhibiting the properties of phenol.

Cholates distilled with excess of alkali yield volatile products passing over from  $150^\circ$  to  $280^\circ$ , and all exhibiting Pettenkofer's bile reaction with sugar and sulphuric acid.

According to Gorup-Bosanez (*Ann. Ch. Pharm.* clvii. 282) cholic acid melted with potassium hydrate, yields acetic and propionic acids, together with a brown insoluble substance exhibiting the characters of dyslysin.

**Reactions with Phosphorous Chloride**.—When powdered cholic acid is digested in phosphorous chloride, much hydrochloric acid is evolved, and a thickish liquid is obtained, from which water precipitates a white resinous mass. When heated with water to boiling, this mass melts and forms on cooling an easily pulverisable lump, which may be purified by boiling it with successive portions of water till the water no longer acquires an acid reaction, dissolving it in warm sodium carbonate, and precipitating it with hydrochloric acid, repeating this several times, and finally digesting it with ether. The product is a peculiar acid containing phosphorus; when dry it presents the appearance of a fine dusty white powder, and, on microscopic examination, is seen to consist of highly refracting granules without any trace of crystals. It has a slightly bitter taste, no smell, is insoluble in water either cold or boiling, soluble in alcohol and chloroform, sparingly soluble in ether. When heated on platinum foil, it melts, becomes brown, takes fire and burns with a greenish flame and emission of thick white fumes, leaving a cinder which burns with difficulty and has a strong acid reaction due to the presence of phosphoric acid. It gives Pettenkofer's reaction with sugar and sulphuric acid.

The numbers obtained from analyses of different portions of the acid nearly correspond with the empirical formula  $C^{27}H^{50}P^1O^{13}$ . If this formula were correct the reaction might be—



There is, however, no guarantee for the purity of the acid, as neither it, nor its salts, can be obtained in the crystalline state. The probable formation of this body by the union of three molecules of cholic acid is extremely interesting when considered in connection with the very high molecular weight by which all the compounds of bile and nerve at present known, are distinguished. It would appear that with the action of tri- or quinquivalent phosphorus, several molecules of non-phosphorised compounds unite to form a condensed molecule containing phosphorus.

**CHOLINE**,  $C^9H^{14}NO^2$ . This base is formed, together with margaramido, glycerophosphoric acid, and small quantities of oleic and margaric acids, when lecithine is left for a month in contact with an equal weight of ammonia (Gobley, *Compt. rend.* **LX.** 1207).

**CHONDRIEN**, or **CHONDROGEN**. Tissues yielding chondrin when boiled with water have been found in the *Brachiopoda*, *Holothuridae*, and *Tunicata*. The mantles of animals of the last-named class, when boiled for some time in a Papin's digester, yield an opalescent solution which, however, does not gelatinise. It is precipitated by acetic acid, the precipitate being insoluble in excess; also by lead-acetate, basic and neutral, and gives a bulky precipitate with alum. The residue left on evaporating the aqueous solution, after treatment with dilute hydrochloric acid and washing with alcohol and water, gives by analysis 14.99 p.c. nitrogen, which agrees nearly with the quantity found in chondrin by Mulder and Scherer (Schüfer, *Ann. Ch. Pharm.* **clx.** 330).

**CHONDRODITE**. See HUMITE.

**CHROME IRON-ORE**. On the analysis of this mineral, see *Chem. News*, **xxiii.** 284; **xxiv.** 304; *Chem. Soc. J.* [2] **ix.** 177).

**CHROMIUM**. In the preparation of this metal by Wöhler's method of reducing chromic chloride with zinc (*1st Suppl.* 910), E. Zettnow (*Pogg. Ann.* **cxliii.** 477) uses as a flux, instead of the mixed chlorides of potassium and sodium recommended by Wöhler, a double chloride of chromium and potassium. He forms this double salt from red potassium chromate, by reducing it with hydrochloric acid in presence of alcohol, and adding chloride of potassium to the boiling liquid, which is then evaporated to dryness. The residue, after being carefully dried, is mixed with finely granulated zinc, and this mixture is introduced by successive portions into a red-hot Hessian crucible, in which, after the last portion has been added, it is heated for half to three-quarters of an hour, and then allowed to cool slowly. The soluble salts are dissolved out by water, the zinc by dilute nitric acid.

**Chromium Trioxide. Chromic Anhydride**,  $CrO^3$ .—For the preparation of this compound in the pure state, the following process is recommended by Zettnow (*Pogg. Ann.* **cxliii.** 474) as the easiest and most economical:—

300 grams of pulverised commercial potassium dichromate are warmed with 500 c.c. of water and 420 c.c. of sulphuric acid, until dissolved; and the solution is left at rest for 10–12 hours, in which time the acid potassium sulphate crystallises out. The mother-liquor is decanted and allowed to drain for an hour or two, the salt being washed with 10–12 c.c. of water. The solution is heated to  $80^{\circ}$ – $90^{\circ}$ , mixed with 150 c.c. of sulphuric acid, and afterwards gradually with the same quantity of water, until the precipitated chromic acid is re-dissolved. The solution is then evaporated until crystals begin to appear. After standing for 10 to 12 hours, the chromic anhydride is precipitated in small, brownish-red crystals. The mother-liquor is decanted from the crystals, again evaporated, and left at rest, whereby a second crop is obtained of rather larger feathery crystals, and in a similar manner a third crop of long scarlet-red needles. These crystals are freed from mother-liquor by draining in a funnel, in the apex of which is placed a piece of thin platinum-foil pierced with very small holes, and finally dried on a porous tile.

To purify the crystallised chromic anhydride thus obtained, it is introduced into a porcelain crucible, and treated gradually with 50 c.c. of pure nitric acid of sp. gr. 1.46 (weaker acid would dissolve the chromic acid), the mixture being thoroughly stirred with a glass rod; it is then placed on a dry tile. If, after standing thus for 12 hours, the chromic anhydride is found to be not thoroughly freed from potash and sulphuric acid, it is sufficient to repeat the operation with 25 c.c. of the nitric acid to remove these impurities. The nitric acid is readily expelled from the crystals by heating on a sand-bath, first gently, then more strongly, until no more acid fumes are evolved.

By this method Zettnow obtained an average of 84.8 p.c. of the theoretical quantity of pure and dry chromic anhydride. By using the green mother-liquor decanted after the third crystallisation, in place of fresh sulphuric acid, a considerable saving is effected, whilst the quantity of chromic anhydride thus procured is about 90.3 p.c. of the theoretical quantity, instead of 84.8 p.c.

*Specific gravity of Chromic Anhydride and of Chromic acid solutions* (Zettnow, *Pogg. Ann.* **cxliii.** 274).—The specific gravity of chromic anhydride was determined by means of commercial benzene, freed from water by digestion with calcium chloride. The dried benzene, whether hot or cold, does not dissolve the smallest quantity of chromic acid.

The sp. gr. of the solid chromic anhydride, as determined by six experiments at 17.5°, was 2.775, 2.777, 2.787, 2.785, 2.804, and 2.800 respectively, the mean being 2.788.

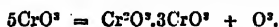
*Specific gravity of Aqueous Chromic acid.*

Percentage of CrO <sup>3</sup> dissolved	Specific gravity of solution	Percentage of CrO <sup>3</sup> dissolved	Specific gravity of solution
62.23 (saturated)	1.7023 at 26°	10.33	1.1569 at 19°
37.82	1.34416 „ 22°	12.34	1.0957 „ 19.5°
	1.3448 „ 19.2°	8.79	1.0694 „ 14.2°
32.59	1.22384 „ 9.7°		1.0679 „ 18°
	1.22100 „ 15.2°	8.25	1.0606 „ 16.2°
	1.21914 „ 18.6°		1.0600 „ 17°
	1.20940 „ 35°		
31.83	1.20714 „ 12°		
	1.20264 „ 20.1°		
	1.20269 „ 20.9°		

*Action of Chromic acid on Carbon compounds.*—Chromic acid in aqueous solution is recommended by Bertholot (*Ann. Chem. Phys.* [4] xxiii. 212) in many cases for the oxidation of organic compounds, instead of the ordinary mixture of potassium dichromate and sulphuric acid, because it acts less violently; in fact, when this mixture is used, the chromic anhydride parts with half its oxygen, producing chrome-alum:



whereas, when aqueous chromic acid is used, only one-fifth of the oxygen of the anhydride is given off, with formation of a chromate of chromium:



By the use of the dilute aqueous acid, *acetylene* is oxidised to acetic acid, and *allylene* to propionic acid. If, however, only a small quantity of water is present, the action on acetylene becomes violent, and the products are formic and carbonic acids.

*Carbon monoxide*, passed through a series of U-tubes filled with pumice-stone moistened with concentrated chromic acid is slowly oxidised to dioxide. *Hydrogen* is also slowly converted into water, when a gypsum-ball steeped in the concentrated acid is introduced into the gas standing over mercury. *Marsh-gas* withstands the action of chromic acid even in the concentrated state. *Ethylene* at ordinary temperatures is completely oxidised to carbon dioxide and water by concentrated solution of chromic acid, and very slowly by dilute solutions (E. Ludwig, *Ann. Ch. Pharm.* clxii. 47).

**Chromates.** *Barium chromates.*—The *dichromate*  $\text{BaCr}^2\text{O}^6 = \text{BaO} \cdot 2\text{CrO}^3$  separates as a yellowish powder from a solution of the normal chromate in boiling aqueous chromic acid. No other acid chromate of barium appears to exist (Zettnow, *Pogg. Ann.* cxlv. 167).

*Chromic Chromate*,  $\text{Cr}^2\text{O}^3 \cdot \text{CrO}^3$  or *Chromium Dioxide*  $\text{CrO}^2$ , is obtained in the hydrated state by mixing a cold solution of potassium dichromate with sodium thiosulphate:



hyposulphuric (dithionic) acid being probably formed in the first instance, and afterwards resolved into sulphurous and sulphuric acids. If the action be completed by aid of heat, and the product washed till the wash-water no longer appears yellow, the compound  $2(\text{Cr}^2\text{O}^3 \cdot \text{CrO}^3) + 9\text{H}^2\text{O}$  is obtained. When dried at a gentle heat, it is a light, bulky, deep-brown powder. It dissolves easily, especially with aid of heat, in dilute sulphuric or hydrochloric acid, forming a green solution; in dilute acetic acid it is less soluble. Nitric acid dissolves it with deep brown colour; strong hydrochloric acid dissolves it, when heated, with evolution of chlorine. From its solutions in dilute sulphuric and hydrochloric acids, ammonia throws down green chromic oxide, while ammonium chromate remains in solution, generally retaining a little chromic oxide. By boiling it with alkaline carbonates, green chromic oxide is separated and an alkaline chromate is dissolved. The compound, when slowly heated, first gives off its water of hydration, and is then resolved, with vivid incandescence, into oxygen and chromic oxide of a fine green colour (O. Popp, *Ann. Ch. Pharm.* clvi. 90).

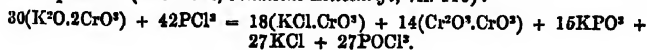
*Mercury-salts.*—Normal mercurous chromate  $(\text{Hg}^2)^2\text{CrO}^6$  is best prepared by

precipitating mercurous nitrate with potassium dichromate; the precipitate is not decomposed by washing with water. On the contrary, the precipitate thrown down by potassium dichromate from *mercuric nitrate* retains the composition of the normal chromate only when washed with dilute nitric acid; if washed with water it loses chromic acid. The only basic mercuric chromate that seems to exist is the tribasic salt  $3\text{HgO} \cdot \text{CrO}_3$  (Freese, *Zeitschr. f. Chem.* [2] vi. 30).

*Nickel-salts.*—Freese (*loc. cit.*), by precipitating a boiling solution of nickel sulphate with neutral potassium chromate, obtained the salt  $3\text{NiO} \cdot \text{CrO}_3 + 6\text{H}_2\text{O}$ . According to E. A. Schmidt (*Zeitschr. f. Chem.* [2] vii. 31), this salt is formed only when the precipitate is thrown down in presence of excess of nickel-salt, as for instance, on mixing boiling solutions of 2 mol. nickel sulphate and 1 mol. potassium chromate. When, on the other hand, the chromate is in excess, precipitates containing less nickel are thrown down under otherwise similar conditions; with 2 mol. potassium chromate and 1 mol. nickel sulphate, Schmidt obtained the salt  $5\text{NiO} \cdot 2\text{CrO}_3 + 12\text{H}_2\text{O}$ , and with 4 mol. of the chromate to 1 mol. of nickel sulphate, the salt,  $2\text{NiO} \cdot \text{CrO}_3 + 6\text{H}_2\text{O}$ . No salt containing less nickel than the last was obtained; on the contrary, by employing 10 or 12 mol. potassium chromate to 1 mol. nickel sulphate, precipitates were thrown down, the composition of which lay between  $5\text{NiO} \cdot 2\text{CrO}_3$  and  $2\text{NiO} \cdot \text{CrO}_3$ . When basic nickel chromate, still moist, is triturated to a thin pulp with ammonia, and gaseous ammonia is passed in till the brown colour completely disappears, *ammonio-nickel chromate* is deposited in the form of a yellowish-green crystalline powder. Further quantities of the same salt are obtained by placing a few crystals of neutral ammonium chromate in the mother-liquor. Large and well-formed prismatic crystals are produced when the ammoniacal solution is covered with a layer of alcohol; they are yellowish-green, dichroic by transmitted light, and undergo decomposition in the air, and more rapidly on warming, giving off ammonia. Malaguti and Sarzeau assign to this salt the formula  $\text{NiO} \cdot \text{CrO}_3 \cdot 3\text{NH}_3 + 4\text{H}_2\text{O}$ ; but Schmidt found it to be anhydrous, and to have the composition expressed by the formula  $\text{NiO} \cdot \text{CrO}_3 \cdot 3\text{NH}_3$ .

*Potassium salts.*—The *dichromate* heated with 2 pts. of strong nitric acid forms a liquid which, on cooling, deposits splendid crimson tabular crystals containing nitric acid, and yielding by analysis 36.4 p.c. chromium, whence may be deduced the formula  $\text{CrO}_2 \cdot \text{OK} \cdot \text{CrO}_3$ , which requires 36.7 p.c. The salt, when heated, gives off red fumes and melts to a blackish-brown liquid. Its aqueous solution yields, on evaporation, not the original salt, but potassium dichromate. An excess of nitric acid appears to convert the salt into  $\text{CrO}_2 \cdot \text{OK} \cdot 2\text{CrO}_3$  (Darmstädter, *Deut. Chem. Ges. Ber.* iv. 167).

The dichromate, heated with *phosphorous chloride* to  $166^\circ$  in a sealed tube, is decomposed, yielding potassium chlorochromate, brown oxide of chromium (chromic chromate), and other products (Michaelis, *Jenaische Zeitschrift*, vii. 110):

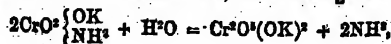


*Potassium Chlorochromate*,  $\text{KCl} \cdot \text{CrO}_3$ , may be obtained in long needles by dissolving the dichromate in three or four parts of warmed strong hydrochloric acid, and recrystallising the product from hot hydrochloric acid; it is partially decomposed by heat, and must be dried *in vacuo*. Dry pure ammonia gas produces with the dry compound, ammonium chloride and a salt crystallisable from hot water, and having

the formula  $\text{CrO}_2 \cdot \text{OK}$ ; its reactions seem to be identical with those of ordinary chromates.

The corresponding *ammonium salt*  $\text{CrO}_2 \cdot \text{ONH}_4$  is produced by passing ammonia gas into a solution of chromyl dichloride,  $\text{CrO}_2\text{Cl}_2$ , in chloroform. It is a brown amorphous powder, difficultly soluble in water, insoluble in alcohol, ether, chloroform, and glacial acetic acid, but readily soluble in mineral acids, from which solutions it separates again as an amorphous powder.

Ether and dry ammonia gas transform potassium chlorochromate into *potassium anido-chromate*  $\text{CrO}_2 \cdot \text{OK} \cdot \text{NH}_2$ , crystallisable from water; cold caustic soda-solution does not decompose this body, but on boiling for some time, ammonia is given off in quantity; on heating it with water to  $100^\circ$  for some hours, the following reaction takes place:—



Similarly nitrous acid gives nitrogen, water, and potassium dichromate. Neither platinum chloride, mercury chloride, nor silver nitrate combines with it.

Together with the amidochromate, a body is formed giving numbers agreeing not very closely with the formula  $\text{Cr}^2\text{O} \cdot \text{NH}^2$ ; it is a chocolate-coloured powder insoluble in water, alcohol, ether, chloroform, and carbon sulphide. Acids and alkalis dissolve it on prolonged heating, the latter with evolution of ammonia. The amount of this body formed is but small, but is increased by allowing the action of the ethereal ammonia to take place under a pressure of 1-2 decimeters of mercury J. Heintze, *J. pr. Chem.* [2] iv. 58, 211).

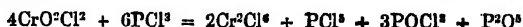
Potassium chlorochromate and potassium cyanide yield gaseous cyanogen chloride and potassium monochromate; with nitrogen tetroxide, the chlorochromate yields nitryl chloride  $\text{NO}^2\text{Cl}$ . The corresponding bromide  $\text{NO}^2\text{Br}$  is obtained by the action of nitrogen tetroxide on potassium bromochromate formed by dissolving potassium dichromate in bromine-water (Heintze).

**Silver Chromates.**—Two only of these salts appear to exist. The normal chromate,  $\text{Ag}^2\text{CrO}_4$ , is always formed when solutions of potassium monochromate and silver-nitrate are mixed, though the appearance of the precipitate varies considerably according as one or the other salt is added in excess. In like manner solutions of potassium dichromate and silver nitrate always yield the pure dichromate of silver  $\text{Ag}^2\text{Cr}_2\text{O}_7$ , or  $\text{Ag}_2\text{O} \cdot 2\text{CrO}_3$ , whether the chromium solution is added in excess or in a mere trace. When silver oxide is heated for some time with solution of normal potassium chromate, the greyish black product, after washing with hot water, consists wholly of silver monochromate. Silver oxide treated in like manner, with solution of potassium dichromate yields pure silver dichromate (Freese).

On the action of Chromates on Ammonia salts. See AMMONIA (p. 61).

**Chromium Oxychlorides.**—Chromyl dichloride,  $\text{CrO}^2\text{Cl}_2$ , is strongly attacked by phosphorous chloride, producing a hissing noise and emission of light.

The reaction is:



(Michaelis, *Jenaische Zeitschrift*, vii. 110).

Chromyl dichloride dissolves in glacial acetic acid, and in chloroform, and ammonia gas passed into the latter solution produces the ammonium salt  $\text{CrO}^2\text{ONH}^4$ , already mentioned, (p. 335).

The chromium chromatochloride, or trichromyl dichloride, described by Thorpe, (1st Suppl. 456) may be regarded as the chloride analogous to this, and represented

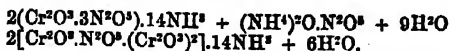
by the formula  $\text{CrO}^2\text{Cl}$  (Heintze, *J. pr. Chem.* [2] iv. 211).

Zettnow (*Pogg. Ann.* cxliii. 328), by heating potassium chlorochromate with sulphuric acid has obtained—together with chromyl dichloride—a brown compound, which after distillation and drying over sulphuric acid, appears to be identical with Thorpe's compound.

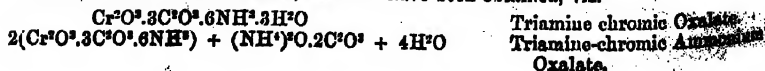
**Ammoniacal Chromium Compounds.** P. T. Cleve (*Sill. Am. J.* [2] xlix. 251), has obtained the following ammonio-chromic compounds, in addition to those previously described (1st Suppl. 452):

$\text{Cr}^2\text{Cl}^2\text{Br}^2 \cdot 8\text{NH}^3 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Chlorobromide.
$\text{Cr}^2\text{Br}^2 \cdot 8\text{NH}^3 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Bromide.
$\text{Cr}^2\text{Br}^2\text{Cl}^2 \cdot 8\text{NH}^3 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Bromochloride.
$\text{Cr}^2\text{Cl}^2\text{I}^2 \cdot 8\text{NH}^3 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Chloriodide.
$\text{Cr}^2\text{I}^2 \cdot 8\text{NH}^3 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Iodide.
$\text{Cr}^2\text{Br}^2\text{O}^2 \cdot 8\text{NH}^3 \cdot 2\text{SO}^2 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Bromosulphate.
$\text{Cr}^2\text{Cl}^2\text{O}^2 \cdot 8\text{NH}^3 \cdot 2\text{CrO}^2 \cdot \text{H}^2\text{O}$	Tetramine-chromic Chlorochromate.
$\text{Cr}^2\text{Cl}^2\text{O}^2 \cdot 8\text{NH}^3 \cdot 2\text{N}^2\text{O}^2 \cdot 2\text{H}^2\text{O}$	Tetramine-chromic Chloronitrate.

Of heptamine-dichromic compounds, only the two following double salts have been obtained:

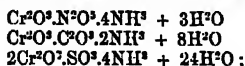


Of salts of the triamine series, two also have been obtained, viz.



The salts of the heptamine and triamine series closely resemble the tetramine salts. The nitrate of the heptamine series is obtained by the action of silver nitrate on tetramine-chromic chloride; the oxalate of the triamine series by the action of oxalic acid on the same chloride.

Besides these three series, Cleve describes the following salts:



but it is doubtful whether they have been obtained in the pure state, inasmuch as they could not be made to crystallise.

#### CHROMO-WULFENITES. See WULFENITES.

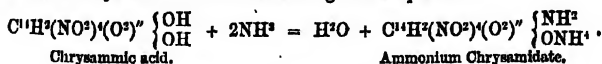
**CHRYSAMMIC ACID**,  $\text{C}^4\text{H}^2\text{N}^2\text{O}^8$ , or  $\text{C}^4\text{H}^2\text{N}^2\text{O}^{12} = \text{C}^4\text{H}^2(\text{NO}^2)_2(\text{HO})_2\text{O}^2$ . Tetranitro-dioxyanthraquinone (1st Suppl. 457). Tilden (*Pharm. J. Trans.* [3] ii. 845) prepares this acid by the action of cold fuming nitric acid on barbaloin, the aloin obtained from Barbadoes aloes, (p. 52). The product is a mixture of aloetic, chrysammic, oxalic and picric acids, the two latter of which are easily dissolved out by cold water, the aloetic and chrysammic acids remaining undissolved. The aloetic acid is finally converted into chrysammic acid by prolonged boiling with nitric acid, and the crystalline precipitate of chrysammic acid, after purification by washing with water, is converted into the potassium salt, which is further purified by recrystallisation. Barbaloin thus treated yields more than one-third of its weight of pure potassium chrysammate.

The acid is obtained by dissolving the potassium salt in boiling water, and strongly acidifying the liquid with acetic acid. It crystallises in thin, yellow, fern-shaped crystals, somewhat resembling picric acid, but more lustrous.

The chrysammates of lead and barium have been described by Schunck and Mulder as red powders, the former containing variable proportions of lead. They may, however, be obtained in a crystalline and perfectly definite state by mixing a solution of the potassium salt with solution of lead or barium acetate acidified with acetic acid. The crystals of the lead salt exhibit a magnificent bronze reflection and strongly polarize transmitted light. The analysis of these salts leads to the formulæ  $\text{C}^4\text{H}^2\text{Pb}(\text{NO}^2)_2\text{O}^4 + 4\text{H}^2\text{O}$  and  $\text{C}^4\text{H}^2\text{Ba}(\text{NO}^2)_2\text{O}^4 + 4\text{H}^2\text{O}$ .

If chrysammic acid has the constitution of tetranitro-dioxyanthraquinone, the substance hitherto called *chrysamide*, which is produced by the action of ammonia on chrysammic acid (i. 955), may be regarded as the ammonium salt of a monobasic acid  $\text{C}^4\text{H}^2(\text{NO}^2)_2(\text{O}^2)^- \left\{ \begin{smallmatrix} \text{NH}^3 \\ \text{OH} \end{smallmatrix} \right.$ , which may be called *chrysamidic acid*\* (tetranitramido-oxyanthraquinone).

The so-called chrysamide is formed according to the equation:



Chrysammic acid.

Ammonium Chrysamidate.

When dry ammonia gas is passed over chrysammic acid, 4.4 p. c. water is given off, according to Mulder; the equation just given requires 4.3 p. c. Strong acids convert the so-called chrysamide into chrysammic acid, whereas by treating it with dilute acids, a body is formed containing more nitrogen than chrysammic acid, evidently free chrysamidic acid (Graebe & Liebermann, *Zeitschr. f. Chem.* [2] vi. 262).

*Hydrochrysamide* (iii. 191), obtained by reduction of chrysammic acid, was regarded by Schunck as  $\text{C}^4\text{H}^3\text{N}^2\text{O}^4$ , or rather  $\text{C}^4\text{H}^{11}\text{N}^2\text{O}^4$ . But from his analyses and from the reactions of this body, it appears rather to consist of  $\text{C}^4\text{H}^{10}\text{N}^2\text{O}^4$ , that is to say of *triamido-nitro-dioxyanthraquinone*  $\text{C}^4\text{H}^3(\text{NH}^2)_2(\text{NO}^2)(\text{O}^2)^-(\text{OH})^+$ . The colourless body formed from chrysamide by further reduction will accordingly be *triamido-nitro-tetraoxyanthracene*  $\text{C}^4\text{H}^3(\text{NH}^2)_2(\text{NO}^2)(\text{OH})^+$ ; it is reconverted into hydrochrysamide by oxidation in the air (Graebe & Liebermann).

**CHRYSANISIC ACID**,  $\text{C}^4\text{H}^3\text{N}^2\text{O}^4$ . Cahours, who first obtained this body by treating nitranisic acid† with fuming nitric acid, and exhausting the product with ammonia in order to separate it from simultaneously formed di- and trinitroanisol,

\* Not the same as Schunck's chrysamidic acid (i. 955).

† In the translation of Cahours' paper in *Lieber's Annalen* it is said that Cahours used 'anisic acid', and the same mistake occurs in *Gmelin's Handbook*, and in the first volume of this Dictionary (p. 267); but Salkowski finds that only nitranisic acid can be converted into chrysanisic acid, and that anisic acid does not yield a trace.

assigned to it the formula,  $C^6H^5N^3O$ , and regarded it as methylated picric acid. Beilstein and Kellner found afterwards that the true formula of this acid is  $C^6H^5N^3O^3$  (1st Suppl. 458), but their researches do not give any clue to its constitution.

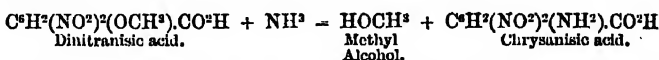
The recent researches of H. Salkowski (*Ann. Ch. Pharm.* clxiii. 1) have shown, however, that it has the constitution of dinitro-amido-benzoic acid  $C^6H^2(NO^2)^2(NH^2).COOH$ . This appears from the following reactions:—

(1). By reduction with tin and hydrochloric acid it is converted into triamido-benzoic acid,  $C^6H^2(NH^2)^3CO^2H$ , which by the action of heat is resolved into carbon dioxide and triamidobenzene,  $C^6H^2(NH^2)^3$ .

(2). By heating chrysanisic acid with fuming hydrochloric acid, it is converted into trichlorobenzoic acid,  $C^6H^2Cl^3.CO^2H$ .

(3). By the action of nitrous acid, a dinitro-oxybenzoic acid,  $C^6H^2(NO^2)^2(OH)CO^2H$ , is obtained; and the same transformation is effected by the action of caustic alkalis.

Chrysanisic acid is not a direct product of the action of nitric acid upon nitranisic acid; it is formed by the action of ammonia on the crude product of the reaction which contains dinitranisic acid, as may be shown by exhausting this crude product with solution of sodium carbonate, precipitating with hydrochloric acid, and recrystallising from alcohol, whereby dinitranisic acid is obtained in pale yellow crystals melting at  $171^\circ-173^\circ$ . This acid dissolves without decomposition in dilute aqueous ammonia, but when boiled for a few minutes with strong ammonia, it is completely converted into chrysanisic acid:



Chrysanisic is therefore *dinitro-para-amido-benzoic acid*, inasmuch as anisic acid is methyl-para-oxybenzoic acid.

Pure chrysanisic acid, prepared according to Cahours' method, melts at  $259^\circ$ , and not, as Cahours states, at a gentle heat. It crystallises from alcohol in small shining rhombic plates, and from hot water in hair-like fasciculated needles. It is very slightly soluble in cold water, but insoluble in dilute acids.

By adding a small quantity of chrysanisic acid, or of one of its salts, to an alcoholic potash solution, an almost black colour is produced, which disappears on standing and quickly on addition of water. This reaction may be used for the detection of the acid; the dark compound formed is perhaps  $C^6H^2(NO^2)^2NHK.CO^2K$ .

*Methyl chrysanisate* is obtained by heating the silver salt with methyl iodide; it crystallises from alcohol in small plates, melting at  $144^\circ$ , and having a metallic-golden lustre.

*Dinitro-amidosalylic, Dinitro-anthranilic*, or more shortly *Chrysalylic acid*, the ortho-isomeride of chrysanisic acid, is produced by the following series of reactions:—

Gaultheria oil treated with a mixture of nitric and sulphuric acids yields methyl dinitrosalyicylate  $C^6H^2(NO^2)^2.OH.CO^2OCH^3$ ; the ammonium salt of this compound mixed with silver nitrate yields the silver salt  $C^6H^2(NO^2)^2.OAg.CO^2CH^3$ ; and by treating this salt with ethyl iodide, the ether  $C^6H^2(NO^2)^2.OC^2H^5.CO^2CH^3$ , is obtained in well-defined monoclinic crystals melting at  $80^\circ$ .

This ether treated with hot ammonia forms a yellow-red solution, together with a solid yellow mass, which, when recrystallised from boiling alcohol, is converted into yellow laminae melting at  $165^\circ$ . The yellow-red solution contains the ammonium salt of dinitro-amido-salylic acid  $C^6H^2(NO^2)^2.NH^2.CO^2H$ , which may be precipitated from it by acids, while the yellow laminae consist of its methyle ether,  $C^6H^2(NO^2)^2.NH^2.CO^2CH^3$ ; the latter may be obtained as sole product of the reaction by using alcoholic instead of aqueous ammonia.

Dinitroamidosalicylic acid is converted into dinitrosalyicylic acid, with evolution of ammonia, by boiling with soda. Its ethylic ether melts at  $135^\circ$ , the methyle ether at  $165^\circ$ . It bears a great resemblance to its isomeride, chrysanisic acid, and has almost the same melting point ( $256^\circ$ ), but the methyl and ethyl derivatives melt at about  $21^\circ$  higher than the corresponding chrysanisic derivatives ( $114^\circ$  and  $144^\circ$ ). Again, the ammonium salt contains one molecule of water, driven off at  $100^\circ$ , whereas that of chrysanisic acid is anhydrous (Salkowski, *Deut. Chem. Ges. Ber.* iv. 870).

**CHRYSENE**,  $C^{18}H^{12}$  (Liebemann, *Ann. Chem. Pharm.* clviii. 209). This hydrocarbon was discovered by Laurent in crude anthracene (i. 958), and further examined by Berthelot, who has produced it synthetically from benzene (1st Suppl. 459). It may be extracted from the mixture of solid hydrocarbons which have a higher boiling point than anthracene, and form the latter portion of the distillate from coal-tar by



treating this mixture with successive quantities of cold carbon sulphide, which dissolves the pyrene and similar hydrocarbons, leaving 18 to 19 per cent. of a yellow powder melting at  $240^{\circ}$ . By crystallising this powder from coal-oil (boiling at  $150^{\circ}$ ) the chrysene is obtained in bright yellow glistening scales, from which the colour cannot be completely removed, even by repeated crystallisation from ether, or by the insolation of its solutions. It is however obtained colourless by heating the yellow crystals with hydriodic acid and amorphous phosphorus to  $240^{\circ}$ ; also by boiling them with alcohol and a small quantity of nitric acid. It cannot be sublimed without decomposition, and when submitted to distillation in a current of gas, its melting point is lowered sometimes as much as  $10^{\circ}$ .

Chrysene is very slightly soluble in cold alcohol, ether, benzene, and glacial acetic acid, but somewhat more soluble in carbon bisulphide. It is moderately soluble in coal-oil of high boiling point when hot, and in boiling glacial acetic acid, from both of which it separates in the crystalline state on cooling. It melts at  $248^{\circ}$ – $250^{\circ}$ , and its boiling point lies above the range of the mercurial thermometer. The yellow chrysene dissolves in a large quantity of hot sulphuric acid, with a dirty violet colour, forming sulpho-acids, whilst colourless chrysene forms a pure blue solution. Chlorine acts upon it very little in the cold, but on heating, a substance is formed which sublimes in white needles with partial decomposition. It forms a *picrate*,  $C^{18}H^{12}.C^6H^2(NO_2)^3O.H$ , crystallising in orange coloured needles, which are decomposed by the action of cold alcohol, being converted into pseudomorphs of chrysene.

By oxidation with chromic acid it is converted into chrysoquinone  $C^{18}H^{10}O^2$ , and by prolonged action into phthalic acid.

*Bromochrysenes*. On adding bromine to chrysene suspended in carbon sulphide, hydrobromic acid is evolved, and a substance is obtained which crystallises from benzene in colourless needles, and appears by analysis to be a mixture of di- and tri-bromochrysene.

*Decachlorochrysene*,  $C^{18}H^2Cl^{10}$ , is formed by heating chrysoquinone (*infra*) for twelve hours with a large excess of phosphorus pentachloride; it is a yellowish uncrystallisable substance soluble in carbon sulphide.

*Nitrochrysenes*.—*Mononitrochrysene*,  $C^{18}H^{11}NO^2$ , is produced by boiling yellow chrysene with alcohol and a little nitric acid of sp. gr. 1.4. The solution slowly acquires an orange colour from formation of nitrochrysene; and if, after 24 hours' digestion, it be separated from unaltered chrysene, concentrated by distillation, and allowed to cool, then filtered and mixed with water, an orange-red precipitate of nitrochrysene is formed, which may be purified by crystallisation from boiling alcohol. The chrysene remaining undissolved in the above operation is much less readily acted upon by nitric acid than before, and when boiled with potash and recrystallised, yields colourless chrysene.

*Tetranitro-chrysene*,  $C^{18}H^5(NO_2)^4$ .—On dissolving chrysene in fuming nitric acid in the cold, and adding water after some hours, this substance is precipitated as a yellow, difficultly soluble powder. By treatment with chromic acid it is in great part destroyed, and when heated to  $170^{\circ}$  with nitric acid, it forms a volatile acid containing nitrogen.

**Chrysoquinone**,  $C^{18}H^{10}(O^2)^2$ . On oxidising crystallised chrysene suspended in glacial acetic by the careful addition of one and a half times its weight of chromic acid, and finally heating to boiling to complete the reaction, a solution is obtained from which the quinone may be precipitated by addition of water, as an orange-red powder. To purify this substance, it is dissolved in concentrated sulphuric acid, filtered through asbestos to separate unaltered chrysene, and precipitated by water; repeated crystallisation from benzene renders it quite pure. It is moderately soluble in hot alcohol, benzene, and glacial acetic acid, and crystallises from the former in long rhombic plates. It is but slightly soluble in ether and carbon sulphide, melts at about  $220^{\circ}$ , and when more strongly heated, sublimes with partial decomposition. It dissolves in cold concentrated sulphuric acid with a fine pure blue colour, and is precipitated unchanged by the addition of water. The production of this blue colour affords a very characteristic test for chrysene. If a mixture of solid hydrocarbons, on oxidation with chromic acid, and subsequent treatment with sulphuric acid, gives the blue reaction, the presence of chrysene may be safely inferred. The quinone of idrialin rents in the same manner gives a red-brown colour. Chrysoquinone yields phthalic acid when treated with potassium permanganate, or subjected to the prolonged action of chromic acid. When it is heated with zinc-powder, chrysene is regenerated.

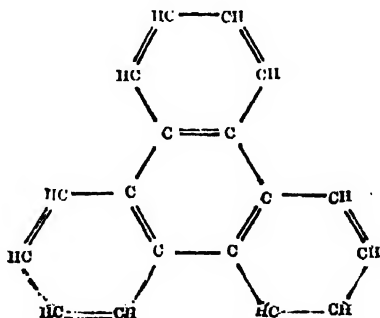
*Dichlorochrysoquinone*,  $C^{18}H^8Cl^2O^2$ .—When 1 mol. of chrysene is heated for a short time to  $200^{\circ}$  with 2 mols. of phosphoric chloride and an excess of phosphorus oxychloride, a green uncrystallisable substance is formed, which is soluble in carbon

sulphide and phosphorus oxychloride, but almost insoluble in alcohol, ether, and benzene. The contents of the tubes, when gradually added to alcohol, give a bright yellow flocculent precipitate of dichlorochrysoquinone.

**Tetranitrochrysoquinone**,  $C^{14}H^2(NO^2)_4O^2$ .—Chrysoquinone dissolves in cold concentrated nitric acid, and after it has been allowed to stand for some hours, water precipitates tetranitrochrysoquinone as an orange-yellow powder, which is but little soluble in most solvents. It deflagrates slightly when heated.

**Chrysohydroquinone**,  $C^{14}H^{10}(OH)^2$ .—Chrysoquinone boiled with zinc-powder and caustic potash-solution, dissolves to a yellow liquid, from which acids precipitate colourless flocks of chrysohydroquinone, which can be easily reoxidised to the quinone. This change takes place when the hydroquinone is heated to  $200^\circ$  with access of air, or when it is dissolved in concentrated sulphuric acid and agitated with air, the solution then acquiring the characteristic blue colour of chrysoquinone.

**Constitution of Chrysene**.—The properties of the derivatives of chrysene, and its conversion into phthalic acid by oxidation, clearly show that it is a member of the naphthalene-anthracene series; and, moreover, the absence of any fatty group is rendered manifest by the formation of the quinone and its reversion into chrysene. Strecker (*Lehrbuch der Organ. Chemie*, 762) has pointed out that its constitution is probably analogous to that of naphthalene and anthracene, and if the substance prepared synthetically from benzene by Berthelot be identical with chrysene, the structure of this hydrocarbon may be represented by the following formula, which indicates that it is formed by the union of three benzene molecules, with elimination of hydrogen:—



**CHRYSOCOLLA. Cupric Silicate**.—This mineral appears to occur on a gneissoid gangue in South Africa, rich in Muscovite and quartz, as a blue layer in botryoidal forms, and carrying here and there a green incrustation. The blue mineral appears also in some places in fibres, apparently crystals, generally mixed with smaller blue crystals. Its analysis gave:

$SiO^2$ (soluble)	$As^2O^3$	$P^2O^5$	$SO^3$	$CO^2$	$CuO$	$Fe^2O^3$	$Al^2O^3$	Gangue	Water
18.82	9.79	11.75	3.45	1.00	32.15	4.36	2.27	10.92	6.41 = 99.92.

It is probably chrysocolla mixed with two minerals, one belonging to the trochantite group, probably langite, the other a cupric arsenophosphate (Maskelyne & Flight, *Chem. Soc. J.* [2] x. 1052).

**CHRYSOPHANIC ACID and CHRYSOPHANINE**. These compounds are contained, according to Bourgoïn, in crude cathartin from senna (p. 270).

Chrysophanic acid is reduced by zinc-dust to anthracene. Whether its formula is  $C^{14}H^{10}O^4$  or  $C^{14}H^8O^4$  is not yet decided. The formula  $C^{14}H^{10}O^4$  is in accordance with the analyses both old and new of chrysophanic acid itself; the formula  $C^{14}H^8O^4$ , on the other hand, is supported by De La Rue and Müller's analyses of diacetyl-chrysophanic acid (1st Suppl. 460) and by Palz's analysis of diacetyl-chrysophanic acid. If the formula  $C^{14}H^{10}O^4$  should be corroborated by further investigations, it will, perhaps, be better to interpret this formula as dioxanthraquinone-dihydrate  $C^{14}H^8(O^2)^2(OH)^2.H^2$ , rather than as tetraoxyanthracene  $C^{14}H^8(OH)^4$ : first, because chrysophanic acid contains only 2 atoms of hydrogen replaceable by acid radicals; secondly, because, it is an acid of quinonic character, and is converted by reducing agents—e.g. by treating its solution in alkalis with sodium-amalgam—into a colourless substance which again

becomes oxidised and coloured on exposure to the air (Graebe u. Liebermann, *Zeitschr. f. Chem.* [2] vi. 261).

**CIMBEX.** The larvæ of *Cimbex variabilis* (living on the leaves of *Alnus incana*) have on both sides of their bodies a series of orifices, from which, on being touched, they squirt a green fluid, which is tasteless and inodorous, has an alkaline reaction, and consists of a moderately concentrated solution of a proteid having great resemblance to albumin.

The nature of the colouring matter (perhaps chlorophyll) has not been ascertained; alkalis change the colour into a yellowish green. The fluid from the larvæ of two other species of cimbex feeding on birch leaves, gave the same results (A. J. von Rossum, *Zeitschr. f. Chem.* [2] vii. 423).

**CIMICIFUGA.** The active principle of Black Snake-root (*Cimicifuga racemosa*) appears to be a neutral, crystallisable body. The fresh root bruised and treated with alcohol produces a tincture which, after the separation of the resin, tannin, &c., by acetate of lead, leaves, on spontaneous evaporation, a powder which may be purified from fatty matter by benzene. The powder freed from the odour of benzene, washed with water, dried, dissolved in alcohol, mixed with pure alumina, and evaporated spontaneously, yields a light dry mass. This mass exhausted with hot alcohol affords a solution which, on evaporation, leaves a crystalline substance having a light yellow colour, and presenting under the microscope an appearance similar to that of rock-candy. The crystals are slightly soluble in ether, more so in alcohol and chloroform, but quite insoluble in benzene, turpentine-oil, and bisulphide of carbon. This substance does not possess the character either of an acid or an alkalioid. It has little taste, on account of its extreme insolubility in the liquids of the mouth, but its solution in alcohol has the intensely acrid and sharp taste which characterises recent cimicifuga (T. B. Courard, *Pharm. J. Trans.* [3] i. 866).

**CINCHONA BARKS** (O. Hesse, *Deut. Chem. Ges. Ber.* iv. 818).—To distinguish between genuine and false cinchona barks, Grahe heats a small piece in a test-tube which is held horizontally; the genuine barks yield a carmine-red tar, but the false barks do not (1st *Suppl.* 461). Batka has shown that this red product is always formed when a cinchona base is heated with cellulose, and this test is therefore very well adapted to prove the existence of alkalioids in the bark; but it cannot be used as a means of distinguishing between genuine and false barks, because there exist genuine barks containing no bases, and false barks in which alkalioids are present. Thus a genuine bark in Hesse's collection (probably from *Cinchona pubescens*) does not contain a trace of any alkalioid, whilst a false bark, which was formerly often found amongst the 'soft bark' (*Cinchona lancifolia* var. *obovata*), and is now found in larger quantities in the market, gives the above reaction, because it contains cinchona bases.

This bark, which Flückiger calls *China cuprea*, has a fine red colour, and gives with ammonia a purple solution, which imparts to filter-paper a fine pink colour after exposure to the air. Nitric and sulphuric acids produce in this solution an amorphous reddish brown precipitate. On filtering, a yellow solution is obtained, which, on adding ammonia, assumes a violet colour, and, after some time, purple amorphous flakes separate out, no doubt a product of decomposition of the tannic acid of the bark. This tannic acid is different from that contained in genuine barks and in *China nova*, as it gives an intense green coloration with ferric chloride. Milk of lime gives, with the bark, a deep yellowish red solution, from which, on exposure to the air, a red lime-compound (cinchona-red lime?) separates. On adding an excess of acetic acid to the filtrate, a gelatinous precipitate is obtained, which cannot be distinguished from that which the genuine barks give under the same circumstances. On filtering from this precipitate and adding basic lead acetate, a copious precipitate of basic lead quinate is formed. The following percentages of bases are contained in this bark:—

	1.	2.	3.	4.
Quinine . . . . .	1.33	1.28	1.20	1.26
Cinchinine (?) . . . . .	—	—	0.46	0.28
Cinchonine . . . . .	—	—	0.22	0.24
Amorphous bases . . . . .	—	—	0.37	0.37

The amorphous bases in this bark gave the same reactions as quinine; quinidine and varisine were not found in it.

Flückiger (*Chem. Centr.* 1872, 152) further points out that *paytine*, a crystallisable alkalioid differing from cinchonine only by the addition of one atom of carbon, is obtained from a so-called false bark, *Quina blanca*.

*Distribution of Alkalioids in Cinchona barks.*—An examination of several species of

cinchona bark by P. Carles (*Pharm. J. Trans.* [3] iv. 643) has led to the conclusion that quinine exists in all parts of the bark, but in a much larger proportion in the external or cortical layers than in the internal or liber layers: in the intermediate layers the proportion diminishes pretty regularly from the exterior to the interior. The seat of the cinchonine has not been so clearly established; it appears, however, in most species, to be more abundant in the outer than in the inner layers.

**CINCHONA BASES. Separation and Estimation.**—J. E. de Vrij (*Pharm. J. Trans.* [3] ii. 624) has given a process for this purpose, based upon the following facts:—

1. The great solubility of quinine and amorphous alkaloid in ether, and the relative insolubility of quinidine, cinchonine, and cinchonidine in this liquid.

2. The great solubility of the iodosulphate of amorphous alkaloid in alcohol, and the very slight solubility of the iodosulphate of quinine (herapathite) in the same.

3. The difference of solubility in water between the tartrate of cinchonidine and the tartrates of cinchonine and quinidine.

4. The difference in solubility between the hydriodide of quinidine and the hydriodide of cinchonine in water and alcohol.

The application of these facts to the determination of the respective cinchona alkaloids is conducted in the following manner:—

5 grams at least of the pulverised mixed alkaloids are digested with 50 grams of ether, and filtered, whereby the alkaloids are separated into two groups.

**A. Part soluble in Ether.**—The ether is evaporated, the residue dissolved in 10 parts of proof spirit acidulated with one-twentieth of sulphuric acid, and alcoholic iodine added until a precipitate is no longer formed. The quinine is thus precipitated as herapathite. One part of herapathite washed, and dried at 100°, represents 0.565 parts of pure quinine. The liquid separated from the herapathite is mixed with an alcoholic solution of sulphurous acid, then neutralised with caustic soda, heated on a water-bath to expel alcohol, and mixed with an excess of soda. The precipitate consists of amorphous alkaloid, with, perhaps, traces of quinidine and cinchonidine.

**B. Part insoluble in Ether.**—The insoluble alkaloids are dissolved in 40 parts of hot water with the aid of a little dilute sulphuric acid, the acid being so adjusted that the solution shall preserve a faint alkaline reaction. To this liquid a solution of Rochelle salt is added, and the whole allowed to remain for twelve hours. The cinchonidine will be found separated as tartrate, which may be collected and dried at 100°. One part of this tartrate represents 0.804 parts of cinchonidine. The filtrate is mixed with a solution of potassium iodide, which precipitates the quinidine as a sandy crystalline powder, provided that the quinidine be not very small in quantity relatively to the cinchonine; otherwise the precipitate is often resinous. One part of the hydriodide dried at 100° represents 0.718 parts of anhydrous quinidine.

The liquid separated from the quinidine is precipitated by caustic soda, whereby the cinchonine is obtained; it is collected and dried as in the previous instances.

The substance designated as 'amorphous alkaloid' is the dextrogyrate base soluble in ether, probably identical with Pasteur's quinine.

On the application of Molecular Rotation to the Estimation of Cinchona bases, see de Vrij (*Pharm. J. Trans.* [3] ii. 1; *Chem. Soc. J.* [2] ix. 857).

#### Periodides of the Cinchona Bases (Jørgensen, *J. pr. Chem.* [2] iii. 146).

The tri-iodide of methylquinine,  $C^{20}H^{24}N^2O^2.CH^3I^3$ , is obtained by adding a solution of 2 atoms of iodine in alcohol to a hot alcoholic solution of the hydriodide of methylquinine. By slow cooling of the liquid the tri-iodide is formed in beautiful black needles, having an adamantine lustre and melting at 159–160°. This body is moderately soluble in alcohol; the brown solution is decolorised by sulphurous acid, sulphuretted hydrogen, and mercury. The tri-iodide, boiled with a large quantity of water, gradually loses the 2 atoms of iodine, and is reduced to methylquinine hydriodide. It does not appear to be decomposed by boiling with strong aqueous ammonia or by cold caustic soda-solution, but it is easily and completely decomposed by solution of silver nitrate.

The following periodides are prepared by corresponding processes and exhibit similar properties:—

#### Tri-iodide of:

		Melting point.
Ethyl-cinchino	$C^{20}H^{24}N^2O^2.C^2H^5I^3$ , like the last	150–151°
Cinchonine	$C^{20}H^{24}N^2O.H.I^3 + aq.$ brown rhombic tables	80–82°
Methyl-cinchonine	$C^{20}H^{24}N^2O.CH^3.I^3$ brown adamantine laminae	161–162°
Ethyl-cinchonine	$C^{20}H^{24}N^2O.C^2H^5.I^3$ dark brown prisms	141–142°
Methyl-quinidine	$C^{20}H^{24}N^2O^2.CH^3.I^3$ brown adamantine laminae	164–165°
Methyl-cinchonidine	$C^{20}H^{24}N^2O.C^2H^5.I^3$ brown hemispherical groups	

When cinchonine tri-iodide is decolorised by gradual addition of a standard solution of sodium thiosulphate complete decoloration takes place, as soon as a quantity of the thiosulphate equivalent to 2 atoms iodine has been added, the salt being then reduced to the hydriodide  $C^{20}H^{24}N^2O.HI$ . This shows that two of the iodine-atoms are in a closer state of combination than the third.

**Quinine and Cinchonine.** *Optical properties.* The specific rotatory power of pure quinine in alcoholic solution is for the yellow ray:

$$\begin{aligned} a_f &= -165.79 \text{ at } 15^\circ \\ &= -162.46 \text{ at } 25^\circ. \end{aligned}$$

The specific rotatory power of quinine in its salts is greater than that of free quinine, the rotation increasing with the proportion of acid present, and with the temperature.

Thus the sulphate gives for the yellow ray the values—

$a_y = -191.47$  in alcoholic solution  
 $a_y = -228.78$  dissolved in 6 molecules of  $H_2SO_4$  diluted till  $SO_3 = 4$  per cent. of the volume:

whence the rotatory powers for the contained quinine are found to be—

$\alpha_y = -220.43$  in alcoholic solution,  
 $\alpha_x = -264.66$  in excess of sulphuric acid.

The mono-acid sulphate gives for the contained quinine:—

$a_v = -264.30$  in alcoholic solution,

or sensibly the same as the acid solution of the sulphate.

With excess of acid, the mono-acid sulphate gives higher values--

With 1 molecule  $\text{SO}_3$ ,  $\alpha_\gamma$  for contained quinine = - 277.23  
 " 3 " " = - 280.77

The diacid sulphate gives—

$$\alpha_y = -287.62.$$

the value being the same whether excess of acid is present or not.

Similarly, the addition of excess of hydrochloric acid raises the rotatory power of the hydrochloride.

Crystallised  $\text{C}^{20}\text{H}^{21}\text{N}^2\text{O}^2 \cdot 2\text{HCl} + 2\text{H}_2\text{O}$ , dissolved in alcohol gave—

in water with large excess of acid  $a_y = -166.41$ ,  
 $a_x = -247.39$ .

The specific rotatory power of cinchonine is:

In alcoholic solution . . . . .	$\alpha_y = + 226.48$
Neutral sulphate in alcoholic solution . . . . .	+ 244.12
" " with 1 mol. free acid . . . . .	+ 261.49
" " " 6 " " " . . . . .	+ 255.86
Hydrochloride in alcoholic solution . . . . .	+ 203.68
" " in strong acid aqueous solution . . . . .	+ 233.12

(Hesse, *Ann. Ch. Pharm.* clxvi. 217).

**Reactions.**—The green coloration produced by *chlorine* and *ammonia* in quinine solutions, is capable of indicating the presence of 1 part of quinine in 4,000 to 6,000 parts of liquid.

*Bromine vapour*, with subsequent addition of ammonia, also produces a green colour, which is perceptible when the solution contains only  $\frac{1}{20,000}$  of quinine.

Vogel's red reaction, obtained by the successive addition of *chlorine, red, or yellow prussiate of potash, and ammonia*, is less delicate, being capable of indicating only about 1 part in 2,500.

Pure quinine hydrochloride dissolves in dilute nitric acid without any marked change of colour, but if it is mixed with 5 p. c. of morphine hydrochloride, an orange-tint is produced; 1 p. c. gives a dark yellow colour, whilst 0.2 p. c. produces a marked change in the tint produced. The acid should contain 20 p. c.  $\text{HNO}_3$  by volume (Hosue, *Ann. Ch. Pharm.* cxlvi. 217).

When cinchonine sulphate is heated in sealed tubes with concentrated hydrochloric acid for some hours to 140°-150°, the contents of the tubes yield crystals not unlike those of cinchonine sulphate, but differing therefrom essentially in their insol-

bility in acids. After one recrystallisation these crystals do not contain a trace of sulphuric acid; their solution is strongly acid, but is no longer fluorescent. They are anhydrous, and contain 3 atoms of chlorine, two of which are readily and completely removed by silver nitrate, the third with difficulty. The mother-liquor from these crystals yields, on further evaporation, a second crop of different aspect, but also free from sulphuric acid.

Quinine sulphate similarly treated gives crystals, which also do not contain any sulphuric acid; they yield a strongly acid solution, which is non-fluorescent, and coloured only very slightly green on addition of chlorine water and ammonia. Potassium ferrocyanide produces a yellow precipitate, insoluble in excess, but soluble on boiling. The base thus formed is precipitated by ammonia, and is readily soluble in ether, also in excess of ammonia and in boiling water. In its behaviour with ammonia and chlorine-water, and with ferrocyanide, it resembles cinchonine; like quinine, it is readily soluble in ether, but differs from both by its solubility in ammonia and in boiling water.

*Action of Quinine in arresting Molecular Movements and Organic Decomposition.*—The active movements in water of fine particles of Indian ink, pure charcoal, finely ground cinnabar, ground parts of plants, fine earth, or, best of all, of the pigment granules of the choroid, observed to go on for days together, are rapidly arrested by a neutral solution of quinine, and the particles are thus caused to subside. A neutral or slightly basic solution of quinine, even in very small quantities, is nearly as powerful in causing this phenomenon of subsidence as alum, more powerful than alum neutralised with sodium carbonate, and still more so than the other officinal salts of the alkaloids. Slight alkaliescence retards the process. It has but little influence over the movements of powdered gamboge.

Quinine also possesses in a remarkable degree the property of preventing the occurrence of certain forms of decomposition. It materially retards the conversion of cane-sugar into glucose, and checks the acid fermentation of flour. The effect of quinine salts, however, in checking acid fermentation does not appear to be due to any peculiar property of the quinine, but to the fact that its neutral salts give off acid. Sulphate of quinine checks the process, but not to a materially greater extent than the corresponding potassium and sodium salts. On the other hand, quinine hydrochloride, like potassium or sodium chloride, rather hastens the process.

Quinine has no effect upon the saccharifying action of saliva; but it energetically checks putrefaction, alcoholic fermentation, and the formation of lactic and butyric acids by the fermentation of sugar.

According to von Boeck, the lessened rate of destruction of albumin in the living body caused by quinine must be ascribed to its direct influence upon (vegetative) cells. The contents of the red blood-corpuscles appear to be influenced by quinine in a similar manner. Quinine is also a muscle-poison (C. Binz, *N. Rep. Pharm.* xxi. 407).

*On the Influence of Quinine on Oxidation in the Blood,* see BLOOD (p. 197).

*Oxidation and Denitrogenation.*—Cinchonine yields by oxidation two compounds containing nitrogen, one of which is an acid, crystallisable, and capable of forming beautifully crystallised salts. This acid treated with nascent hydrogen gives up its nitrogen and becomes changed into another strong tribasic acid, free from nitrogen, crystallisable, and very like certain plant-acids in its general properties. The second compound formed by the oxidation of cinchonine is also crystallisable, but it has not been much examined.

These compounds are different from all the oxidation-products of cinchonine hitherto described. From their composition it seems to follow that cinchonine  $C^{20}H^{21}N^2O$ , is composed of two atomic groups, one containing  $C^{11}$  the other  $C^9$ ; and that the acid whose nitrogen is removable is derived from the  $C^{11}$  group, the other from the  $C^9$  group,—which also contains the same number of carbon-atoms as chinoline (H. Weidel, *Deut. Chem. Ges. Ber.* vi. 555).

When quinine is distilled with zinc and zinc-sodium, a distillate is obtained which is free from nitrogen, and smells like cumin oil, while sodium cyanide is found in the residue. Similar results are obtained with cinchonine (J. Boeko, *ibid.* 488).

*Hydrobromides of Quinine and Cinchonine.* Neutral Quinine Hydrobromide,  $C^{20}H^{21}N^2O \cdot 2HBr + 3H^2O$ , is obtained by mixing 10 parts of quinine sulphate with 50 parts alcohol (85 p. c.), adding the mixture, after warming, to a solution of 8 parts potassium bromide, 20 parts water, and 10 parts dilute sulphuric acid (1 mol: 100), heating the whole to boiling, filtering after a few minutes, and then evaporating a little. Part of the salt then crystallises on cooling and the rest may be obtained by leaving the solution to evaporate. It forms white, opaque or translucent nacreous crystals, very soluble in water, and in alcohol, and having an acid reaction. A basic salt is obtained by using 5 parts potassium bromide and 5 parts dilute

sulphuric acid (1 : 100) to 10 parts quinine sulphate. It is likewise formed from the neutral salt by dissolving 1 part of the latter in 10 parts of dilute alcohol (equal volumes of alcohol and water), mixing the warmed solution with ammonia to slight alkaline reaction, and then with a solution of  $\frac{1}{2}$  part of the neutral salt. On heating the liquid to boiling and leaving it to cool, the basic salt separates in radiate groups of crystals having the lustre of asbestos. It is very soluble in alcohol, less soluble in water: the solution is alkaline.

*Neutral Cinchonine Hydrobromide*,  $C^{20}H^{21}N^2O \cdot 2HBr$ , may be prepared by double decomposition, better however, by the method described for the quinine salt (10 parts basic cinchonine sulphate, 50 parts alcohol, 8 parts potassium bromide, 10 parts water, and 20 parts dilute sulphuric acid); a small quantity of basic salt which forms at the same time, must be removed by filtration. The neutral hydrobromide forms rhombohedral crystals, very soluble in water and in alcohol, but less so than the quinine salt; it has an acid reaction. A *basic cinchonine hydrobromide* is prepared in the same manner as the corresponding quinine salt. The evaporated alcoholic solution is mixed with a little water, and the salt which separates is crystallised from hot water. Or  $\frac{1}{2}$  of a solution of the neutral salt is neutralised with ammonia, and the remaining third then added. The basic hydrobromide forms long shining needles which dissolve easily in alcohol, and have an acid reaction.

*Solubility of Cinchonine in Alcohol and Chloroform*.—According to Oudemans (*Zeitschr. anal. Chem.* xi. 287) cinchonine is much less soluble in pure alcohol and pure chloroform than in mixtures of the two. At  $17^\circ$  a mixture of 4 parts alcohol and 1 part chloroform takes up a maximum quantity, which is seven times as large as that taken up by absolute alcohol, and twenty times as large as that dissolved by pure chloroform.

• *Quinine Sulphates*. *Normal quinine sulphate* crystallises from water with  $7\frac{1}{2}H^2O$ ; probably, however, it contains  $8H^2O$ , but is very efflorescent; from alcohol it crystallises with only  $2H^2O$ .

*Mono-acid quinine sulphate* contains  $C^{20}H^{21}N^2O^2 \cdot H^2SO^4 + 7H^2O$ . Six-sevenths of the water of crystallisation is given off in the exsiccator; the last seventh at  $100^\circ$ – $115^\circ$ ; the salt dissolves in 11 parts of water at  $13^\circ$ , and is less soluble in alcohol. The *di-acid sulphate* contains  $C^{20}H^{21}N^2O^2 \cdot 2H^2SO^4 + 7H^2O$  (Hesse. *Ann. Ch. Pharm.* clxvi. 217).

**Cinchonidine**. For the optical rotatory power of this base, Hesse finds the following values:

- $\alpha_D = -112.49$  for the base dissolved in alcohol,  
 $\quad \quad -178.47$  for that contained in the sulphate dissolved in alcohol.

The presence of free sulphuric acid slightly diminishes the rotation.

For the hydrochloride:

- $\alpha_D = -162$  in alcoholic solution,  
 $\quad \quad = -169.29$  with excess of acid.

The *hydrochloride* crystallises in monoclinic double pyramids containing 1 mol. water; this form is not exhibited by the hydrochloride of any other cinchona alkaloid. By evaporation of the solution at a moderate heat, or by crystallisation from a very concentrated solution, asbestos-like crystals of a dihydrate,  $C^{20}H^{21}N^2O \cdot HCl + 2H^2O$ , are obtained; but these, when left for a considerable time in the mother-liquor, gradually disappear, and the solution afterwards deposits the more compact crystals of the monohydrate.

*Cinchonidine sulphate* crystallised from alcohol has the composition  $2C^{20}H^{21}N^2O \cdot H^2SO^4 + 2H^2O$ .

**Quinidine or Conchinine** (Hesse),  $C^{20}H^{21}N^2O^2$ . This alkaloid may be prepared from quinoidine by a method depending on the difficult solubility of its acid tartrate, 100 grams of quinoidine are dissolved in 200 grams of water holding in solution 50 grams of tartaric acid, and the liquid, after brisk agitation is set aside for several days. A mass of crystals then forms which is to be pressed between folds of linen, dissolved in 14 times its weight of water, and the solution filtered while hot. Acid tartrate of quinoidine then crystallises out, and is easily purified (De Vrij, *Chem. Cent.* 1872, 152).

According to Hesse (*Ann. Chem. Pharm.* clxvi. 237) the product thus obtained contains a mixture of the tartrates of several cinchona alkaloids, from which however the quinidine may be separated by recrystallising the crude product from boiling water, dissolving the resulting crystals in hot water, and neutralising with ammonia. The

solution on cooling deposits neutral tartrate of cinchonidine, sometimes mixed with neutral tartrate of quinine, while the quinidine remains in the mother-liquor, and may be precipitated therefrom by heating with potassium iodide.

For the optical rotatory power of quinidine Pasteur found  $\alpha_D = + 250.75$  at  $13^\circ$ , which is equivalent to  $\alpha_D = + 327$ . According to Hesse, it is much smaller, viz.

$$\alpha_D = + 260.65.$$

The sulphate  $2C^{20}H^{21}N^2O^7 \cdot 2H^2SO + 2H^2O$ , gives for the alkaloid contained in it nearly the same value, viz.:

$$\alpha_D = + 261.18,$$

but in presence of 1 and 6 molecules of acid, it gives the values:

$$\alpha_D = + 323.06$$

and

$$\alpha_D = + 324.54.$$

The hydrochloride gives for the rotatory power of the alkaloid contained in it:

In alcoholic solution . . . . .	$\alpha_D = + 270.03$
In aqueous solution with excess of dilute acid . . . . .	$\alpha_D = + 312.47$
Dissolved in fuming acid . . . . .	$\alpha_D = + 257.52.$

**Quinicine and Cinchonine.** These bases, isomeric with quinine and cinchonine respectively, were discovered by Pasteur, who obtained them by heating the sulphate or other salt of quinine, quinidine, cinchonine or cinchonidine. He observed, however, that to make the transformation complete, and prevent decomposition, the heat must be moderate and the salt must be kept for some time in a viscous or resinous state, and that the change is best effected by heating the sulphate to  $120^\circ$ – $130^\circ$  with a little water and sulphuric acid (i. 971; v. 13). These observations have lately been confirmed by D. Howard (*Chem. Soc. J.* [2] x. 102), who finds that the action of heat on a solution of a salt of cinchona alkaloid in water in sealed tubes, even when exposed to a higher temperature than is required under favourable circumstances to convert it wholly into the isomeric modification, is very slight indeed; if however, a considerable excess of acid be present, the alkaloid, is, under the same circumstances, slowly changed, but far less readily than when Pasteur's conditions are observed. On the other hand, a mixture of glycerin and neutral cinchonine sulphate exposed to the needful heat, is converted into sulphate of cinchonine at the same rate as with a mixture of the salt with acid. Quinine sulphate when heated with glycerin showed no signs of the formation of quinicine, owing apparently to the slight solubility of the salt in that medium.

The change in the alkaloids is accompanied in all cases by the development of a yellow colour, which seems inherent in the resulting alkaloid; if more heat is used than is absolutely needed, especially when atmospheric air is present, a further decomposition takes place, with formation of a darker colour; this may be in great part prevented by heating in an atmosphere of carbonic anhydride.

Quinicine is contained in the impure quinine salts which crystallise from the mother-liquors of the manufacture of quinine sulphate, and is most conveniently prepared by purifying the alkaloids contained in the mother-liquor from the recrystallisation of those impure products, by solution in ether, then evaporating the ether, dissolving the residue together with oxalic acid, in the smallest possible quantity of water, and leaving the solution to crystallise.

The base separated by potash or soda from the oxalate thus obtained is a yellowish oil, which cannot be obtained pure in the solid state, for it will not bear heat without decomposition, and holds water too strongly for drying in a vacuum. It has a peculiar bitter taste, much less intense and permanent than that of the other cinchona-alkaloids; is very soluble in alcohol, soluble to a large extent in ether, from which it separates as an oil when the ether is allowed to evaporate. It is a strong base; the salts are neutral to test-paper; a small excess of the base strongly restores the colour of reddened litmus. Ammonia precipitates its solutions but imperfectly, whence it would appear to be even a stronger base than quinine.

Chlorine-water, followed by ammonia, produces in solutions of its salts the green colour and precipitate of dallocchin which distinguishes quinine and quinidine. Strong acids, even in the cold, produce a change of colour, and even when diluted with a considerable quantity of water; heat renders the action much more rapid. This coloration is strongest when nitric acid is used, an excess of which, with the aid of heat, develops a strong yellow-green colour, even in a weak solution. In this reaction, as well as in the persistent colour of its salts, quinicine shows a strong resemblance to aricine.

Quinicine salts are very soluble and difficult to crystallise, but the platino-chloride, oxalate, and acid tartrate, crystallise with comparative facility and can be obtained



pure. The salts of quinine prepared from quinine are exactly similar in their properties to those prepared from quinidine; in fact, there is but one quinine, from which ever of the isomeric bases it is derived.

The *platino-chloride*,  $C^{20}H^{24}N^2O^2 \cdot 2HCl \cdot PtCl_4$ , precipitated from a hot solution, forms a crystalline powder; from a hot acid solution it separates, on cooling, in definite crystals. The *oxalate*  $2C^{20}H^{24}N^2O^2 \cdot C^2H^2O^4 + 9H^2O$  crystallises easily, but is difficult to purify completely, on account of the facility with which it changes under the influence of air, light, or heat. It is extremely soluble in water, the wet crystals melting at  $100^\circ$ , but much less so in cold water; insoluble in ether, but very soluble in alcohol, and to a less degree in amyl alcohol, from hot concentrated solutions in either of which solvents it crystallises freely on cooling. The water of crystallisation is partially given off *in vacuo*, and entirely at  $100^\circ$  after previous drying; if the salt is at once heated to  $100^\circ$  without previous exsiccation, it is apt to fuse.

The *acid tartrate*,  $C^{20}H^{24}N^2O^2 \cdot C^2H^2O^6 + 6H^2O$ , crystallises freely from strong solutions in radiated needles, which melt easily at  $100^\circ$ . By gradual drying at about  $50^\circ$  it loses 4 mols. water, and at  $140^\circ$  the remaining 2 mols. are expelled, with fusion and slight discoloration.

The *sulphate*, *citrate*, *hydrochloride*, *phosphate*, and *acetate* are all exceedingly soluble in water; on evaporation *in vacuo* they form semi-crystalline masses. The *hydrobromide* and *ferricyanide* obtained by double decomposition form oily strata at the bottom of the solution, soluble in an additional quantity of water, but show no sign of crystallisation even on long standing. The *hydriodide* also forms an oily stratum in strong solutions, but on standing it becomes semi-solid by formation of crystals; weaker solutions also deposit a small quantity of flocculent crystals, but in neither case can they be separated from the mother-liquor. The *sulphocyanate* also forms an oil when in concentrated solutions, but crystallises from a somewhat larger quantity of water in long silky needles, almost white, very soluble, and readily decomposed by heat.

The leaves of *Cinchona succubra* have been found by J. E. Howard to contain minute quantities of an alkaloid which is soluble in ether, and is precipitated in the crystalline form by an alcoholic solution of oxalic acid. Whether this alkaloid is identical with quinine must be decided by further investigation.

Cinchonidine and its salts are very similar to quinine and its salts; the base is soluble in ether, separating, like quinine, as an oily layer at the bottom of the solution as the ether evaporates. Its salts are somewhat more soluble than the corresponding quinine salts. The same similarity is observed between those prepared from cinchonine and those from cinchonidine that is found between the salts of quinine prepared from quinine and from quinidine.

The *platinochloride* has the composition  $C^{20}H^{24}N^2O^2 \cdot 2HCl \cdot PtCl_4$ .

The *oxalate*,  $2C^{20}H^{24}N^2O^2 \cdot C^2H^2O^4 + 7H^2O$ , differs from the oxalate of quinine by containing only 7 mols. of water; it very readily loses a portion of this water, and is therefore difficult to dry for analysis; the whole is given off at  $100^\circ$ . No definite point of hydration is reached by drying in a vacuum. It is somewhat more soluble than the quinine salts.

The *acid tartrate*,  $C^{20}H^{24}N^2O^2 \cdot C^2H^2O^6 + H^2O$ , crystallises in crusts composed of short prisms, which lose their water at  $120^\circ$  without fusion.

The action of these alkaloids on polarised light also shows the identity of the alkaloid produced by the action of heat on the isomeric alkaloids, the different action on the polarised ray disappearing with the other characteristic distinctions. Quinine, either from the strongly levogyrate quinine, or from the dextrogyrate quinidine, exhibits a comparatively feeble right-handed rotation, identical within the limits of errors of observation.

The observed molecular rotatory powers of these alkaloids for the yellow ray are as follows:—

In a spirituous solution of the alkaloid—

Quinine from quinine gives . . . .	$\alpha_D = +39^\circ$
Quinine from quinidine . . . .	$\alpha_D = +39^\circ$
Quinine from quinoidine . . . .	$\alpha_D = +39.3^\circ$

Oxalate of quinine in an acid solution—

Prepared from quinine . . . .	$\alpha_D = +13.4^\circ$
Prepared from quinidine . . . .	$\alpha_D = +14^\circ$
Prepared from quinoidine . . . .	$\alpha_D = +14^\circ$

Cinchonidine in a spirituous solution—

Prepared from cinchonine . . . .	$\alpha_D = +48^\circ$
Prepared from cinchonidine . . . .	$\alpha_D = +48.4^\circ$

## Oxalate of cinchonine in an acid solution—

From cinchonino . . . . .	$\alpha_D = +18^\circ$
From cinchonidino . . . . .	$\alpha_D = +17.0^\circ$

The rotatory power in both cases is much less in an acid solution than in a spirituous solution of the alkaloid.

**Amorphous Alkaloid of Cinchona bark.**—It is not known with certainty whether this alkaloid, sometimes called quinoïdino (v. 26), is quinine or another alkaloid really uncrystallisable. Hitherto the most careful purification has failed to obtain crystalline salts from it such as have been described. When quinine is present, it will, as has been stated, crystallise out of the mixture, but the bulk of the quinoïdine, however carefully purified, refuses to crystallise, even after many months' standing. It seems highly improbable, though of course it is possible, that this is owing to some impurity which hinders the crystallisation: for we find that quinine-salts prepared from crystallisable alkaloid crystallise entirely with comparative freedom, even when the heat used in its formation has been considerably above the point needed, and sufficient to decompose a portion, and there is no sign of any amorphous modification being formed.

Quinoïdine closely resembles quinine in other respects. When purified, as far as possible, by fractional precipitation and solution in ether, it forms a readily fusible yellow resin. The platinumchloride precipitates as an amorphous powder, readily fusible, slightly soluble in hot water, and much more so in hot dilute hydrochloric acid, from its solution in which it is deposited, on cooling, as an amorphous powder which, under the microscope, appears to consist of globules without any sign of crystallisation.

The salt precipitated from a cold solution contains 26.59 p.c. of platinum, and after solution in dilute acid 26.28 p.c.; it is, therefore, isomeric with quinine and quinine.

It is difficult to speak with certainty of the optical properties of this alkaloid, on account of the great difficulty of insuring absolute purity from the other alkaloids of higher rotatory power, a very small percentage of which would evidently vitiate the results. The specimen, the analysis of the platinum salt of which is given above, showed a specific rotatory power of  $+33^\circ$ ; other specimens gave higher results, but their purity was more doubtful (Howard).

See further, Hesse (*Ann. Ch. Pharm.* clxvi. 273).

**Quinamine,  $C^{20}H^{27}N^2O^2$ .** (Hesse, *Deut. Chem. Ges. Ber.* iv. 985).—This alkaloid occurs, together with paricine and several others, in the bark of *Cinchona succirubra*, now extensively cultivated in India. The quantity of it contained in the bark is, however, extremely small, so that its preparation is very difficult.

The whole of the alkaloids contained in the bark are first extracted by the ordinary methods, then dissolved in dilute sulphuric acid; the warm solution is neutralised with ammonia, and potassium-sodic tartrate is added, which throws down cinchonidine and quinine, if present, in the form of neutral tartrate. The filtered solution is treated with ammonia to liberate the bases, and then shaken with ether, which takes up the quinamine, together with the amorphous substances, including paricine, but leaves the greater part of the cinchonine undissolved. The separated ethereal solution left to evaporate slowly in a tall glass vessel, first deposits short prisms of cinchonine, then very long delicate prisms of quinamine, and finally leaves an amorphous mass which must be removed as completely as possible by inverting the vessel while it is still fluid, afterwards breaking off the neck, and removing the adhering amorphous particles from the sides with filter-paper.

The crystalline mass thus obtained is rinsed with dilute alcohol, the residue dissolved in dilute hydrochloric acid, and platinum chloride added as long as it produces a permanent precipitate. From this precipitate the quinamine may be directly separated by ammonia; but it is better to remove the platinum by hydrogen sulphide, and then, after expelling the excess of that gas, to precipitate the quinamine by ammonia. It is finally purified by recrystallisation from boiling alcohol. The quantity obtained is for the most part very small, rarely amounting to 0.1 p.c. of the bark; in one case, 0.3 p.c. was obtained.

Quinamine crystallises in delicate, asbestiform, anhydrous prisms, easily soluble in strong alcohol, ether, and light petroleum oil, slightly soluble in dilute alcohol, insoluble in water and in alkaline solutions. Its alcoholic solution is alkaline and neutralises acids. Quinamine melts at  $172^\circ$  and crystallises again, on cooling, in radiated masses. Continued heating, however, renders it brown and amorphous. Its optical rotatory power is  $\alpha_D = +106.8$ .

**Hydriodide of quinamine,  $C^{20}H^{27}N^2O^2$ ,** forms colourless anhydrous prisms easily soluble in boiling, sparingly in cold water; the neutral sulphate is easily soluble in water and crystallises with difficulty in six-sided prisms and short laminae. The

hydrochloride, acetate, neutral and acid tartrate, mercurio-chloride, mercurio-iodide, and auro-chloride, are amorphous; the platino-chloride is extremely soluble in water, so that it is only in very highly concentrated solutions of the hydrochloride that a precipitate is formed by platine chloride.

**Paricine** (Hesse, *Ann. Ch. Pharm.* clxvi. 283).—This alkaloid, first found by Winkler in 1845, in a false cinchona bark said to be imported from Peru, afterwards in the bark of a true cinchona, viz. *C. lutea*, occurs also in the bark of *U. succirubra*. When the alkalis have been separated from this bark in the usual way, and the aqueous solution of the mixed sulphates is treated with strong nitric acid, paricine nitrate is thrown down in yellowish flocks. To separate the base, this precipitate, which becomes resinous, is kneaded with nitric acid, the mass drained with alcohol, ammonia added to decompose the nitrate, and the solution treated with hot petroleum oil, which abstracts the alkaloid from the alcoholic solution. The petroleum oil is then evaporated off, the residue dissolved in dilute hydrochloric acid, and the solution, after purification with animal charcoal, is mixed with ammonia, which throws down a yellowish-white flocculent precipitate of pure paricine.

Paricine dissolves easily in ether, alcohol, and light petroleum oil, but is nearly insoluble in water and ammonia. It cakes together at  $100^{\circ}$ , and melts at  $116^{\circ}$ . It dissolves easily in strong sulphuric acid. Strong nitric acid converts it into a dark-green resin, which dissolves with deep yellow colour on warming. Its solution in acetic acid gives, with nitric acid or sodium nitrate, a yellowish-white precipitate of paricine nitrate. The same solution gives precipitates with sodium chloride and potassium iodide. The chlorides of gold, mercury, and platinum produce flocculent precipitates in the solution of paricine in hydrochloric acid.

Paricine has not yet been obtained in sufficient amount for quantitative analysis.

**Aricine.** The existence of this alkaloid, obtained, according to Pelletier & Corriol, from a white cinchona bark from Arica (*1st Suppl.* 357), is regarded by Hesse as still doubtful (*Ann. Ch. Pharm.* clxxvi. 259).

**Paytine**,  $C^{21}H^{24}N^2O$ . Hesse (*Ann. Ch. Pharm.* cliv. 287; clxvi. 272). This is an alkaloid obtained from a white cinchona bark from Payta in Peru. It is prepared by exhausting the bark with alcohol, evaporating, supersaturating the residue with sodium carbonate, and then agitating it with ether. The ethereal solution is treated with dilute sulphuric acid to convert the base into a sulphate, and the acid solution, after being nearly neutralised with ammonia, is mixed with potassium iodide, whereby the base is precipitated as a hydriodide, which is decomposed by sodium carbonate and agitated with ether. On leaving the ethereal solution to evaporate, the base remains in beautiful crystals containing  $C^{21}H^{24}N^2O.H^2O$ .

Paytine has a bitter taste; it is not poisonous; its optical rotatory power is  $\alpha_D = -49.5$ . It dissolves easily in ether, benzene, chloroform, light petroleum oil, and alcohol, sparingly in water, potash, and ammonia. From alcohol it crystallises in beautiful colourless rhombic crystals exhibiting the combinations  $OP \cdot \infty P \cdot \infty P\infty$ , with  $mP\infty$  subordinate; the alcoholic solution reddens blue litmus-paper. Paytine melts at  $156^{\circ}$  and at a higher temperature gives off a colourless oil, and leaves a carbonaceous residue. When distilled with soda-lime, it gives off a non-azotised body, paytone, which sublimates in colourless laminae or needles, dissolves easily in alcohol and ether, and reacts indifferently with dilute sulphuric or nitric acid, potash-solution, and alcohol.

Paytine forms salts with dilute acids. The hydrochloride,  $C^{21}H^{24}N^2O.HCl$ , forms colourless prisms soluble in 16.6 parts of water at  $15^{\circ}$ ; it is easily soluble also in alcohol, but insoluble in ether.

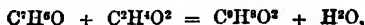
The platino-chloride is a dark yellow amorphous precipitate which must be rapidly filtered and washed, as it is very liable to decompose.

The mercurio-chloride is a yellowish amorphous powder. The hydriodide crystallises in white prisms soluble in water nearly insoluble in alcohol. The nitrate crystallises in needles, and can be prepared only by double decomposition with the hydrochloride and silver nitrate.

Paytine gives various coloured reactions. The platinum precipitate, heated with hydrochloric acid, dissolves with brown-red colour, quickly changing to blue, a blue precipitate being formed at the same time; auric chloride colours the solution of the hydrochloride purple-red and forms a precipitate of the same colour. Solution of bleaching powder produces in the acid solution, first a dark red, then a blue colour, which quickly disappears, the liquid then turning pale yellow and depositing a white amorphous body.

White cinchona bark yields also an amorphous alkaloid which Hesse regards as amorphous paytine.

**CINNAMIC ACID**,  $C^9H^8O^2$ , is formed by heating benzoic aldehyde with acetic acid and a small quantity of gaseous hydrogen chloride, or with zinc chloride, to  $160^\circ$ :



The quantity of cinnamic acid thus obtained is but small. If a larger quantity of hydrochloric acid is used, or greater heat applied, a certain quantity of metacinnameno is always formed by the action of the hydrochloric acid on the cinnamic acid (H. Schiff, *Zeitschr. f. Chem.* [2] vi. 700).

Crude cinnamic acid prepared from storax always contains a rosin, sometimes also benzoic acid. It may be purified by adding water and ammonium carbonate, stirring the liquid, leaving it to stand for some time, then precipitating with hydrochloric acid, and distilling the dried precipitate. Benzoic acid then volatilises first, and afterwards (between  $280^\circ$  and  $290^\circ$ ) cinnamic acid, which may be freed from an adhering oily substance by pressure between filter-paper, or recrystallisable from alcohol (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2] vii. 489).

**Nitro-cinnamic acids.**—Cinnamic acid yields two isomeric nitro-acids which may be obtained from it by the action of fuming nitric acid. The *para-acid* is easily obtained pure, and it is very sparingly soluble in alcohol. It forms slender needles melting at  $165^\circ$ . The other modification is much more soluble in alcohol, and was formerly mistaken for a mixture of benzoic acid, nitrobenzoic acid, and other oxidation-products of cinnamic acid.

The *barium salt of the para-acid*,  $Ba[C^9H^4(NO^2)O^2]^2 + 3H^2O$ , crystallises from water in microscopic yellow needles, sparingly soluble in cold water, and giving off nearly all their water over oil of vitriol, the last portion ( $\frac{1}{4}H^2O$ ) at  $150^\circ$ . The *calcium salt*  $Ca[C^9H^4(NO^2)O^2]^2 + 2H^2O$  forms short flat shining needles. The *ethylic ether*  $C^9H^4(NO^2)(C^2H^5)O^2$  crystallises from alcohol in fine, very thin, slightly yellowish needles: it melts at  $138.5^\circ$  (at  $136^\circ$  according to Mitscherlich), dissolves very slightly in boiling ether, scarcely at all in cold ether.

By dissolving para-nitrocinnamic acid in sodium carbonate and passing chlorine into the liquid,  $\beta$  *nitro-phenyl-chlorolactic acid*  $C^9H^4(NO^2)ClO^2$  is formed; this acid melts at  $166^\circ$ , and is more soluble in water and more stable than chlorophenyl-lactic acid (Beilstein a. Kuhlberg).

**Nitro-hydrocinnamic acid**, which, according to Glaser and Buchanan, softens when heated, and becomes perfectly liquid at  $153^\circ$ , is a mixture of two isomerides, of which the *para-acid* can be easily obtained pure by recrystallisation from water, being less soluble than the other nitro-acid. It forms small flat needles melting at  $163^\circ$ – $164^\circ$ . The *barium salt* of the crude acid forms a semi-fluid mass, whereas that of the pure *para-acid* crystallises in microscopic needles, containing, like the calcium salt, 2 molecules of water. The *ethylic ether*  $C^9H^4(NO^2)(C^2H^5)O^2$  forms long, flat crystals melting at  $33^\circ$ – $34^\circ$ .

Para-nitro-cinnamic and para-nitro-hydrocinnamic acids are converted by oxidation with chromic acid mixture into para-nitrobenzoic acid (Beilstein a. Kuhlberg).

**CITRACONIC ACID**,  $C^8H^6O^4$ . *Barium salt.*—When neutral ammonium citraconate and barium acetate are mixed together in the cold, an amorphous precipitate is thrown down, which becomes crystalline by prolonged heating. The same salt is obtained by heating aqueous citraconic acid with barium acetate. In the crystalline state, it is quite insoluble in water, and has the composition  $2C^8H^4BaO^4.5H^2O$  (Kümmerer, *Ann. Ch. Pharm.* clxx. 191).

**Brominated Derivatives.**—Citraconic anhydride heated to  $140^\circ$  with dry bromine, is converted into bromocitraconic anhydride,  $C^8H^4BrO^4$ . The same compound is produced, together with bromoxaform (p. 213), by the action of bromine on pyrotartaric acid. The action is very slow at ordinary temperatures, but when 13 parts pyrotartaric acid, 24 parts bromine, and 10 cub. cent. of water are heated together to  $120^\circ$ , the bromine disappears after two hours, and on cooling, there is obtained a pale yellow liquid and usually a white crystalline mass of bromocitraconic anhydride. On mixing the liquid with 4 or 5 times its volume of water, crystals of bromoxaform separate after a while, and the liquid filtered therefrom yields, on agitation with ether, an additional quantity of bromocitraconic anhydride, which by recrystallisation from water, pressure, and final crystallisation from ether, may be obtained in the form of white crystals. Its formation appears to be due to the splitting up of dibromopyrotartaric acid (the formation of which has not, however, been actually observed) according to the equation:



It is also formed, together with a dark-coloured unctuous substance, when pyro-

taric acid is heated to  $100^{\circ}$  with dry bromine (Lagermark, *Zeitschr. f. Chem.* [2] vi. 299).

Bromocitraconic anhydride melts at  $97^{\circ}$ – $98^{\circ}$ , begins to volatilise a little above its melting point, distils with aqueous vapour, and boils without decomposition at about  $200^{\circ}$  (Lagermark),  $225^{\circ}$  (Kekulé). It is soluble in water, hydrobromic acid, alcohol, ether, carbon sulphide, and chloroform, and crystallises unaltered from hydrobromic acid, ether, or carbon sulphide, in large six-sided apparently rhombic plates (Lagermark). It dissolves slowly in cold, quickly in warm water, with formation of bromocitraconic acid,  $C^3H^3BrO^4$ ; but from boiling water it separates without alteration in shining laminae; this results from the facility with which bromocitraconic acid splits up into water and the anhydride, this decomposition taking place even when the acid is evaporated over oil of vitriol (Kekulé).

When bromocitraconic anhydride is heated with water and sodium-amalgam, the liquid contains pyrotartaric acid, together with the unaltered anhydride (Lagermark).

Ammonium Bromocitraconate,  $C^3H^3Br(NH^4)^2O^4$ , is anhydrous, easily soluble in water, insoluble in ether and in absolute alcohol. The potassium salt  $C^3H^3BrK^2O^4$ , is a white deliquescent mass insoluble in absolute alcohol. The barium salt  $C^3H^3BrBaO^4$  forms tufts of microscopic prisms; the calcium salt  $C^3H^3BrCaO^4 + 2H^2O$ , gives off part of its water at  $140^{\circ}$ , the rest at  $160^{\circ}$ , and remains undecomposed at  $180^{\circ}$ . The silver salt  $C^3H^3BrAg^2O^4$  is formed as a white, quickly crystallising precipitate, when a solution of bromocitraconic anhydride, neutralised with ammonia, is mixed with silver nitrate (Kekulé). According to Lagermark, it blackens at  $100^{\circ}$  and turns dark brown when boiled with water.

By the action of bromine and water on pyrotartaric acid, Lagermark obtained, besides bromoxanform and bromocitraconic anhydride, a nearly colourless acid which agreed very nearly with bromocitraconic acid, but could not be obtained pure. It melted more easily, and decomposed at the boiling point of the anhydride. A tarry substance was also formed.

**CITRIC ACID,  $C^3H^3O^7$ .** This acid is found in large quantity in the leaves of the wild cherry, *Cerasus acida* (Tschoder, *Zeitschr. f. Chem.* [2] vi. 176.)

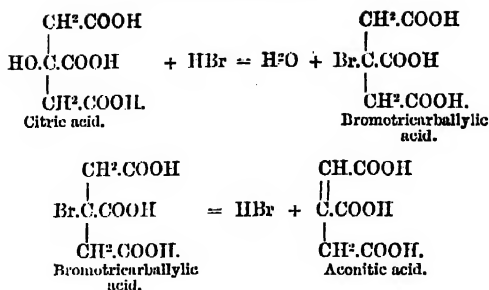
Citric acid crystallises from a solution which has not been heated above  $100^{\circ}$  with one molecule of water, which it loses in the air, or more quickly at  $130^{\circ}$ . When the substance dried at  $130^{\circ}$  is re-dissolved in water, or when an aqueous concentrated solution of the acid is boiled for some time, anhydrous crystals are obtained, which appear to be an isomeric modification of common citric acid. By heating ordinary ethyl citrate,  $C^6H^5(C^2H^3)^2O^7$ , with alcoholic ammonia to  $70^{\circ}$ – $110^{\circ}$  for 24 hours, citramethane,  $C^6H^5(NH^2)^2(C^2H^3O)^2O^4$ , is formed as a dark green amorphous and hygroscopic powder, which is soluble in water and alcohol, but not in ether, and may be used as a colouring matter (Saradinaki, *Deut. Chem. Ges. Ber.* vi. 496).

**Action of Hydrobromic acid** (Mercadante, *Gazzetta chimica italiana*, i. 248). When pulverised citric acid dried at  $100^{\circ}$  is dissolved in three times its weight of hydrobromic acid boiling at  $126^{\circ}$ , and heated for 12 hours in a flask with reversed condenser, a crystalline product is obtained, free from bromine, and yielding, when dissolved in alcohol and treated with gaseous hydrochloric acid, a product which is resolved by water into a heavy oil and an aqueous solution of citric acid. No brominated acid is obtained by this reaction.

The oil dried with calcium chloride and distilled, boils almost constantly at  $275^{\circ}$ ; it is slightly yellow, has a characteristic aromatic odour, and yields by analysis 55.09 p.c. C., and 7.19 H., numbers agreeing nearly with the formula of aconitic ether  $C^8H^{11}O^6$ , which requires 55.81 C., 6.97 H., and 37.22 O. Aconitic ether is said, however, by Crasso (i. 55) to boil at a much lower temperature, viz., at  $236^{\circ}$ . But Mercadante, on preparing aconitic ether by saturating a solution of aconitic acid in absolute alcohol with hydrochloric acid gas, obtained an oily liquid which began to boil at  $255^{\circ}$ , and passed over for the most part between  $270^{\circ}$  and  $275^{\circ}$ , this latter portion exhibiting all the characters of the product obtained as above by the action of hydrobromic acid on citric acid. It is probable that the aconitic ether examined by Crasso was mixed with itaconic ether, inasmuch as, in preparing aconitic acid by the action of heat on citric acid, it is impossible to obtain a product quite free from itaconic acid.

The action of hydriodic acid on citric acid does not yield definite results. Dessaignes has shown that aconitic acid is formed by boiling citric acid for a long time with hydrochloric acid.

The formation of aconitic acid by the action of hydracids on citric acid consists in the elimination of a molecule of water, and may be represented by the following equations:—



*Action of Permanganates.*—Citric treated with potassium permanganate, forms a solution which leaves an uncrystallisable syrup on evaporation. No acetone is formed, as is the case when citric acid is decomposed in presence of free acid (A. Fleischer, *Dent. Chem. Ges. Ber.* v. 350).

*Distinction of Citric acid from other Fruit-acids.* Kümmerer (*Zeitschr. anal. Chem.* viii. 298) detects citric acid in presence of tartaric or malic acid, by means of the barium salt to be described further on. The solution of the acids is mixed with excess of barium acetate, and the amorphous precipitate is heated for several hours with the liquid in a covered vessel on the water-bath. The precipitate, which is bulky at first, usually diminishes greatly in volume in about two hours, becoming heavy and granular, and being completely converted into the microcrystalline salt,  $\text{Ba}^2(\text{C}^3\text{H}_5\text{O}_7)^2 + 7\text{H}^2\text{O}$ . The filtrate, mixed with lead acetate, does not yield any precipitate of lead citrate. Any bases that may be present in the liquid, such as lime, iron oxide, &c., must be removed, and the filtrate neutralised, before adding the barium acetate. Very dilute solutions must be evaporated to a small bulk, after precipitation with the barium salt; otherwise the needle-shaped salt  $\text{Ba}^2(\text{C}^3\text{H}_5\text{O}_7)^2 + 5\text{H}^2\text{O}$  will be formed instead of the preceding. 50 grams of a solution of 1 gram sodium acetate,  $(2\text{Na}^+\text{C}^2\text{H}_3\text{O}_2^- + 11\text{H}^2\text{O})$ , mixed with barium acetate, did not give an immediate precipitate; but on heating the liquid, an amorphous precipitate was formed which, in a short time became aciculate-crystalline, and after further concentration passed into the characteristic monoclinic form.

Neutral ammonium citrate added to a hot solution of *basic ferric chloride* throws down a light yellow precipitate which redissolves completely in excess of the citrate; hence it is that solutions of citrates often give no precipitate with ferric chloride. Sodium citrate reacts in the same manner as the ammonium salt; the yellow iron-compound is often formed only after some minutes, and still increases after several hours. Hence it follows that citric acid and aconitic acid cannot be distinguished from one another by their behaviour with ferric chloride; still less can they be separated by this re-agent, since the ferric citrate precipitated is always mixed with aconitate (Kümmerer).

Lead citrate, precipitated from the sodium salt with excess of lead nitrate, melts in the boiling liquid to a single kneadable lump, which, on prolonged heating or on cooling, is resolved into a powder of  $\text{Pb}^2(\text{C}^3\text{H}_5\text{O}_7)^2 + 3\text{H}^2\text{O}$ , having a vitreous lustre. Diammonio tartrate and the corresponding sodium salt form, with lead nitrate, precipitates which behave in a similar manner when quickly heated. From malate of lead, the citrate and tartrate differ only by not forming a clear liquid. If, however, the malic acid is not quite pure, its lead salt exactly resembles the citrate or tartrate (Kümmerer).

*Examination of Citric acid for Crystals of Tartaric acid.*—The following methods for this purpose are given by Lager (*Dingl. polyt. J.* cxi. 387):—1. A solution of 4 grams potassium hydrate in 60 c.c. water is mixed with 30 c.c. of 90 p.c. spirits of wine, and poured on one or two glass plates, so that the liquid stands not less than 6 mm. high. Small and large crystals of the citric acid to be tested are now placed in the solution, about 3 to 5 centimeters distant from one another. The plates are on no account to be disturbed. In two or three hours the citric acid crystals are nearly, if not quite dissolved, and in each of their places is left a small, delicate, white, powdery patch. The tartaric acid crystals, on the contrary, appear dissolved to a small extent only, whitish and opaque, and with either an enclosure of white acicular crystals, or surrounded by an aggregate of small crystalline groups lying one upon another. The citric acid crystals, after being subjected for several minutes to the action of the alkaline solution, appear clearer and more transparent, the tartaric acid crystals remain and whitish.

2. The crystals are placed, with the same precautions, in a dilute, transparent solution of potassium permanganate, made strongly alkaline by addition of fused potassium hydrate. After one or two hours, tartaric acid crystals, which as a rule are not quite dissolved, will be found to have left a yellow or colourless spot. Citric acid, on the contrary, gives a green colour, with a tinge of blue; the crystals are usually dissolved. The first plan is the best and safest; in either case the mode of procedure described must be strictly adhered to, or the results will be considerably modified. Perfectly pure citric acid gives no whitish spots, but the commercial acid never fails to do so.

**Quantitative estimation.**—J. Crouse (*Pharm. J. Trans.* [3] ii. 547) gives a process for the estimation of citric acid, depending upon the precipitation of an alkaline citrate by barium acetate, the resulting barium citrate being perfectly insoluble in alcohol of sp. gr. .805, while the alkaline acetates and barium acetate are freely soluble in that liquid. The presence of alkaline acetates does not in any way interfere with the reaction. If the citric acid is already in combination with an alkali, one or two grams of the salt are dissolved in 20 c. c. of water, and the solution exactly neutralised with ammonia or acetic acid as may be required; a slight excess of barium acetate is then added, and afterwards twice its volume of alcohol of 95°. The whole is then allowed to remain undisturbed for 24 hours. The barium citrate, which at first resembles a thick jelly, has by that time become denser and easier to wash. The precipitate is then thrown on a filter, washed with alcohol of 63°, and dried at a moderate heat.

To obtain accurate results, it is necessary to estimate the barium in the precipitated citrate. The filter is therefore burnt, and the ashes, together with the precipitate, gently ignited with a few drops of sulphuric acid, until a constant weight is obtained. Every three molecules of barium sulphate obtained represent one molecule of citric acid.

\* When it is required to estimate the citric acid of a non-alkaline citrate, soluble or otherwise, a certain weight of the salt is first heated carefully with a solution of caustic potash, the heat being applied long enough to decompose the salt thoroughly, but not to such an extent as to alter the citric acid. The liquid is then filtered, and the filtrate, after neutralisation with acetic acid, treated as a solution of an alkaline citrate.

Crouse likewise describes briefly a peculiar class of citrates in which an alkaline citrate plays the part of a base, a certain metallic salt, the part of an acid: thus, phosphate hypophosphite, valerate of iron, &c., were found to dissolve readily in solutions of the alkaline citrates, losing thereby, more or less completely, their special characteristics as salts of iron.

**Metallic Citrates** (Kümmerer, *Ann. Ch. Pharm.* cxlviii. 294; clxx. 176).—The trisodic salt  $2Na^+C^3H^3O^7 + 11H^+O$ , which usually crystallises in large rhombic prisms, has also been obtained by Kümmerer in fine, silky, concentrically grouped needles. All attempts to prepare sodio-potassic citrates by saturating citric acid with mixtures of the corresponding carbonates were unsuccessful, the trisodic salt always crystallising out, while the deliquescent tripotassic salt remained in solution.

**Barium salts.**—By precipitating sodium citrate with calcium chloride or by saturating citric acid with laryta water, an amorphous precipitate is formed which has the composition  $Ba^+(C^3H^3O^7)^2 + 7H^+O$ , and when heated in the water-bath with a large quantity of water, is converted into the microcrystalline salt  $Ba^+(C^3H^3O^7)^2 + 5H^+O$ , consisting of uniformly thin, concentrically grouped needles. The same salt is gradually deposited in microscopic, short, thick prisms, from a solution of 2 mols. trisodic citrate and 3 mols. barium acetate in a quantity of water such that 150 grams of water are present to 1 gram of the barium acetate. By heating the pentahydrated salt with water, or either of the preceding salts with aqueous ammonia, the *hebario salt*  $Ba^+(C^3H^3O^7)^2 + 7H^+O$  is obtained in well-defined microscopic monoclinic prisms. The same salt is formed as an amorphous precipitate on mixing free citric acid with barium acetate in a solution diluted to the degree above mentioned.

**Strontium salts.**—When 2 grams of trisodic citrate and 8 grams of strontium acetate are dissolved in 500 grams of water at ordinary temperatures, a precipitate begins to form after 24 hours, goes on increasing for several days, and settles at the bottom of the vessel in loose lumps or a network of silky microscopic needles having the composition  $Sr^+(C^3H^3O^7)^2 + 5H^+O$ . It is not altered by digestion with aqueous ammonia.

When citric acid is heated for some time with strontium acetate and water, the precipitate, which is at first amorphous, becomes crystalline, and appears under the microscope to consist of monoclinic tablets. The salt thus obtained has the composition  $Sr^+H^+(C^3H^3O^7)^2$  or  $2Sr^+(C^3H^3O^7)^2 + 11H^+O$ . When this salt is heated for several hours with strong acetic acid, the residue contains short microscopic prisms

having the same composition, while the acetic acid solution deposits the salt  $2\text{S}_2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^1 + 5\text{H}^2\text{O}$ , apparently in the amorphous state.

**Calcium salts.**—By precipitating sodium citrate with calcium chloride, or saturating citric acid with lime-water, a precipitate of the salt  $\text{Ca}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 4\text{H}^2\text{O}$  is obtained which does not appear distinctly crystalline under the microscope, but, when heated in the water-bath, is converted, without change of composition, into a mass of transparent microscopic needles. The same change takes place on dissolving the amorphous precipitate in acetic acid, and leaving the solution to evaporate. This salt dissolves in aqueous ammonia and separates from the solution unaltered, even after prolonged digestion in the water-bath.

A solution of 1 part calcium acetate in 300 parts water, mixed with half the quantity of sodium citrate necessary to precipitate the whole as trisodic salt, slowly deposits the salt  $\text{Ca}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 7\text{H}^2\text{O}$  in the form of a precipitate having an almost gummy aspect, but appearing under the microscope to consist of short prisms. It gives off 4 mols. water over sulphuric acid, and 6 mols. at  $210^\circ$ . The tetrahydrated salt above described gives off the whole of its water at  $200^\circ$ .

**Magnesium salts.**—The salt  $\text{Mg}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 8\text{H}^2\text{O}$ , or  $\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)$ ,  $\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 8\text{H}^2\text{O}$ , is obtained by digesting a boiling solution of citric acid with excess of magnesium carbonate. By mixing the solutions of magnesium sulphate and trisodic citrate, or by boiling magnesium acetate and citric acid together in alcoholic solution, the salt  $\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 9\text{H}^2\text{O}$  is obtained in microscopic six-sided prisms, with pyramidal summits; and by dissolving this salt in hot water and evaporating, oblique prisms are obtained having the composition  $2\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 11\text{H}^2\text{O}$ .

By mixing magnesium acetate and citric acid in aqueous solution and adding alcohol, the salt  $\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 14\text{H}^2\text{O}$  described by Heldt (1st Suppl. 998) is obtained as a tenacious precipitate, which gradually solidifies to crystalline crusts.

Solutions of sodium citrate and magnesium acetate mixed and evaporated, yield an acid solution and a tenacious mass, which is very soluble in water and has an alkaline reaction. This solution, heated in a closed vessel, deposits a microcrystalline precipitate containing  $\text{Mg}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 13\text{H}^2\text{O} = 4\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 3\text{H}^2\text{O}$ .

Trimagnesium citrate dissolves in hot aqueous ammonia and separates from the solution on evaporation as a crystalline precipitate containing  $\text{Mg}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 9\text{H}^2\text{O}$ , and the filtrate, on further concentration, yields the salt  $\text{Mg}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 3\text{H}^2\text{O}$ , or  $2\text{Mg}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 3\text{H}^2\text{O}$ .

**Zinc salts.**—The salt  $\text{Zn}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 2\text{H}^2\text{O}$ , described by Heldt as a crystalline powder, was obtained by Künmerer in microscopic monoclinic prisms. A basic salt  $\text{Zn}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2$ , similar to the last-mentioned magnesium salt, was obtained by dissolving the trimetallic salt in aqueous ammonia and evaporating. By prolonged contact with acetic acid it is gradually converted into the crystalline trimetallic salt. From all the zinc citrates the zinc is but imperfectly precipitated by sodium carbonates, even after prolonged heating.

**Cadmium salts.**—When a hot solution of trisodic citrate is poured into a hot solution of cadmium sulphate till a permanent precipitate is formed, this precipitate, which is at first amorphous, melts under the hot liquid to a soft mass, which, after several hours heating in the liquid, is converted into microscopic prisms of the salt  $2\text{Cd}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + \text{H}^2\text{O}$ , perfectly insoluble in cold water. Cold solutions of the same two salts yield an amorphous precipitate which, when left under the liquid, changes into microscopic rhombic prisms. The amorphous salt melts when heated with water; the crystalline salt does not. This salt has the composition  $\text{Cd}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 10\text{H}^2\text{O}$ ; at  $150^\circ$  it gives off the greater part of its water, and is converted into the former hydrate  $2\text{Cd}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + \text{H}^2\text{O}$ ; at  $200^\circ$  it becomes anhydrous. By concentrating the filtrate, crystalline deposits are obtained which, under the microscope, appear to consist partly of needle-shaped prisms, partly of monoclinic prisms, very much like the two forms of the barium salt  $2\text{Ba}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 7\text{H}^2\text{O}$ . By treatment with ammonia, the trisodic citrate is converted into the basic salt  $\text{Cd}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2$ , with 18 and 27 mols. of water, the latter crystallising from the mother-liquor of the former.

**Copper salts.**—The solution of cupric carbonate in citric acid deposits, on boiling, a green crystalline precipitate consisting of  $2\text{Cu}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 8\text{H}^2\text{O}$ . When cupric carbonate is treated with cold aqueous citric acid, and the filtered solution is mixed with alcohol, a faintly greenish-blue bulky precipitate is formed, which, after drying between filter-paper, is still quite soluble in water. Its formula is  $\text{Cu}^2\text{H}^2(\text{C}^2\text{H}^4\text{O}^7)^2 + 15\text{H}^2\text{O}$ . The dry salt turns green at  $100^\circ$ , is converted into acetonate at  $160^\circ$ , and decomposes quickly on further heating. It also decomposes gradually if kept in the alcoholic liquid in which it has been formed. On heating the aqueous solution, the whole of the copper is thrown down in the form of the dicupric salt above mentioned.



the supernatant liquid becoming quite colourless, and exhibiting a strong acid reaction. The pentacupric salt decomposes gradually also, even when kept in the dry state in perfectly closed vessels, changing its colour and being resolved into the dicupric salt, free citric acid, and water.

When 1 mol. citric acid is heated with 2 mols. cupric sulphate in very dilute solution, a considerable quantity of the dicupric salt is precipitated; and, on filtering, after the liquid has begun to bump violently, and heating the filtrate, a further quantity of the salt is precipitated. This precipitation may be repeated several times, the reaction taking place as represented by the equation:



The ammoniacal solution of the dicupric salt yields, by evaporation, blue easily soluble crystalline crusts, the aqueous solution of which quickly gives off ammonia when heated, and leaves the original salt.

**Lead salts.**—The salt  $Pl^2(C^3H^4O^7)^2 + 3H^2O$  is obtained by adding sodium citrate to lead acetate, and digesting the precipitate with water or acetic acid, or more quickly and in larger crystals having a vitreous lustre, by precipitating sodium citrate with a large excess of lead nitrate. When the precipitate formed in the cold is heated with the supernatant liquid, it melts to a soft coherent mass, like malate of lead, and, after longer heating, is resolved into a mass of highly lustrous crystals having the same composition. The triplumbic salt, heated with ammonia, is converted into the amorphous diplumbic salt  $Pl^2(C^3H^4O^7) + 2H^2O$ .

**Iron salts.**—A *ferrous citrate*  $FeH^2(C^3H^4O^7) + H^2O$  is produced by boiling metallic iron with citric acid; it forms a heavy white powder consisting of microscopic rhombic tablets. By mixing an aqueous solution of ferric acetate with citric acid and alcohol, a light yellow precipitate of *ferric citrate* is obtained, easily soluble in water, but not deliquescent.

**Manganese salts.**—The salt  $MnH(C^3H^4O^7) + H^2O$ , described by Holdt, is easily obtained by digesting manganous carbonate with a slight excess of citric acid. The *trimanganous salt*  $Mn^3(C^3H^4O^7)^3 + 9H^2O$  crystallises in distorted rhombic prisms of a light rose colour. At 130° it gives off its water, and is immediately converted into aconitate. If it be then heated to 150°, it detonates, whereas in its original state it may be heated to 210° without decomposition. From the filtrate of citric acid, saturated in the cold with manganous carbonate, the salts  $Mn^3H^3(C^3H^4O^7)^3 + 15H^2O$ , or  $Mn^4(C^3H^4O^7)^4 \cdot Mn^2(C^3H^4O^7) + 15H^2O$ , crystallises on evaporation in microscopic monoclinic tablets. From the mother-liquors of trimanganous citrate, the salt  $Mn^4H^4(C^3H^4O^7)^4 + 18H^2O$ , or  $Mn^4(C^3H^4O^7)^4 \cdot 2Mn^2(C^3H^4O^7) + 18H^2O$  may be prepared. The pure *dimanganous salt*  $Mn^2(C^3H^4O^7)$  appears also to exist.

The composition of many of the citrates above described, affords further evidence of the tetrabasic character of citric acid (see 1st Suppl. p. 473).

**CITRON and CITRONELLA OILS.** See OILS, VOLATILE.

**CITRUS LIMONUM.** See LEMON.

**CLADONIC ACID.** This name is given by Stenhouse (*Ann. Ch. Pharm.* clv. 50) to the acid obtained from *Cladonia rangiferina*. This acid was formerly regarded as identical with usnic acid till Hesse (*ibid.* cxvii. 346) showed that it differs therefrom by its melting point, which is 176°. Hesse named it  $\beta$ -usnic acid. Stenhouse finds that it yields, by dry distillation,  $\beta$ -orcin, which is not obtained from usnic acid.

**CLANDESTINA.** The flower-buds of *Clandestina rectiflora*—a plant which flowers in early spring at the foot of the Pyrenees—yield to ether two crystalline substances, one yellow, and resembling cholesterol in other respects, the other called clandestinin, white, soluble in alcohol, quite insoluble in water and in dilute acids (Hartsen, *Chem. Centr.* 1872, 524).

**CLAY.** *Estimation of the Fire-resisting qualities of Clays.*—E. Richters (*Dingl. polyt. J.* cxcl. 50, 150, 229; *Jahresh.* 1860, 1074) estimates the fire-resisting qualities of clays by determining how much alumina must be added to a comparatively fusible clay, and how much silica to a refractory clay, so that at certain temperatures (as high as possible) it may exhibit the properties of a normal clay. (The criterion adopted is that the samples, after being heated for two hours to the melting point of wrought iron, shall appear but slightly glazed). The degree of fire-resisting power thus determined is represented by the quantity of quartz or alumina, expressed in tenths of the weight in clay, required to produce the result above mentioned, the addition of alumina being denoted by the sign —, and that of quartz by +.

2nd Sup.

A A

The following are the results of experiments made by this method:—

1. In white clay from Saarau (in Middle Silesia) containing on the average 53 p.c. of quartz-sand removable by levigation, the fire-resisting power was found equal to — 2 (this clay served for the preparation of the normal clay, by adding to it  $\frac{2}{10}$  of its weight of pure alumina obtained in the preparation of soda from cryolite).
2. The same clay after levigation; + 2.
3. Blue clay from Saarau; + 2.
4. Another blue clay from the same locality;  $\pm$  to — 1.
5. A clay from Valendar near Coblenz; — 1; (the last three on account of their great cohesion could not be levigated).
6. Clay from Mirow (Poland) with 12.7 p.c. sand; — 3.
7. Clay from Grojecc (Poland) with 8.2 p.c. sand; — 3 to 4.
8. Clay from Poremba (Poland) with 20.03 p.c. sand; — 4.
9. Clay from Bielschowitz (Upper Silesia) with 27.7 p.c. sand; — 4.
10. Clay from Czielze with 15.94 p.c. sand; — 5 to 6.
11. Clay from Tillendorf (Silesia) with 30.11 p.c. sand; — 3.
12. Whitish-grey clay from Comprachezütz with 35.91 p.c. sand; — 4 to 5.
13. Blue clay from the same locality with 31.24 p.c. sand; — 6;
14. Blue clay from Brieg, with 26.15 p.c. sand; — 6.
15. White-grey clay from the same locality with 33.34 p.c. sand; — 5.
16. Argillaceous schist from Mettkau (Silesia), with 74.81 p.c. sand; various according to the fineness of the powder.

The chemical analysis of these clays gave the following results, the fine quartz-powder removed, together with the clay, by levigation, being reckoned with the sand:—

	1	2	3	4	5	6	7	8
Al <sub>2</sub> O <sub>3</sub> . . . . .	17.31	39.34	35.70	32.66	33.47	27.62	25.51	20.82
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.56	1.28	1.01	3.23	4.60	1.87	2.13	1.91
CaO . . . . .	—	—	trace	0.50	0.93	0.56	0.43	0.51
MgO . . . . .	—	—	—	—	0.67	0.73	1.15	0.64
K <sub>2</sub> O . . . . .	0.46	1.04	1.11	1.56	1.18	2.25	2.20	2.20
Na <sub>2</sub> O . . . . .	—	—	—	—	—	—	—	—
SiO <sub>2</sub> (combined) . . . . .	19.00	45.39	38.29	36.21	38.21	31.21	35.34	29.47
Sand . . . . .	55.89	—	4.40	14.20	9.34	29.39	25.46	37.15
Water . . . . .	5.70	12.95	19.49	11.64	11.81	6.27	6.87	6.17
	99.91	100.00	100.00	100.00	100.21	99.90	99.18	98.90

	9	10	11	12	13	14	15	16
Al <sub>2</sub> O <sub>3</sub> . . . . .	20.40	21.60	20.97	15.83	17.05	16.96	16.48	7.88
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2.98	5.69	1.35	1.86	3.60	3.70	2.58	1.80
CaO . . . . .	0.34	0.31	—	trace	0.79	0.98	0.74	0.07
MgO . . . . .	0.61	0.74	0.15	0.41	1.08	1.22	0.98	—
K <sub>2</sub> O . . . . .	1.20	2.25	0.32	trace	1.00	1.89	1.48	1.14
Na <sub>2</sub> O . . . . .	0.59	—	0.32	0.90	1.28	0.50	0.40	trace
SiO <sub>2</sub> (combined) . . . . .	32.14	32.68	27.31	23.05	23.65	21.14	22.32	10.84
Sand . . . . .	35.68	30.51	42.20	50.61	45.10	48.31	40.16	76.01
Water . . . . .	6.06	6.39	6.08	6.25	6.08	5.30	4.91	2.81
	100.00	100.20	98.50	98.91	99.63	100.00	100.00	100.00

C. Bischof gives two methods of estimating the fire-resisting qualities of clays: 1. By determining the quantity of a normal mixture of pure silica and alumina which must be added to the clay, to render it infusible at a certain high temperature (*Diag. polyt. J. exciv. 420; excviii. 396*).

2. By Chemical Analysis (*ibid.* cc. 110 and 280).

(1). The first method is similar in principle to that of Richters, but is regarded by Bischof as more accurate. Small cylinders of the clay to be examined, are twice heated to the melting point of platinum; the cylinder is then weighed, crushed, and mixed with a test-substance consisting of 2 parts of pure alumina and 1 part of pure silica. This test-substance is added in proportions of  $\frac{1}{10}$  of the weight of the cylinder.

the cylinder being heated to the melting point of platinum after each addition. This treatment is repeated until the cylinder remains unglazed and the structure becomes granulated. The pyrometric value of the clay is estimated by the quantity of the test-material required, this quantity varying from  $\frac{3}{10}$  to  $\frac{10}{10}$  of the weight of the cylinder.

(2). In judging of the fire-resisting qualities of clays from their chemical composition regard must be had: 1. To the proportion of the alumina and fluxes (*i.e.* the alkalis, alkaline earths, and ferrous oxide); 2. To the proportion of alumina and silica—

A clay is more refractory the greater the quantity of alumina which it contains in proportion to the fluxes, and the smaller the quantity of silica in proportion to the alumina. A simple expression for the relative pyrometric value may be obtained by dividing the number (A) which expresses the proportion of the silica and alumina taken together—*i.e.* of the aluminium silicate or true clay—to 1 part of the fluxes, by the number (B) which expresses the proportion of silica to 1 part of alumina.

The following table exhibits the composition of seven kinds of fire-clay, together with their relative fire-resisting powers, as directly determined by the first method; and, lastly, the quotients calculated from the chemical composition by the method just explained:—

*Composition and Fire-Resisting Power of Clays.*

	Formula	Fire-resisting power	Quotient $\frac{A}{B}$
<b>CLASS I.</b>			
a. Clay from Saarau, selected: purest and most refractory variety	$19.25(Al_2O_3 \cdot 1.38SiO_2) + RO$	100	$\frac{19.25}{1.38} = 13.95$
b. Average sample of clay from the same locality . . . . .	$16.59(Al_2O_3 \cdot 1.69SiO_2) + RO$	100	$\frac{16.59}{1.69} = 9.70$
<b>CLASS II.</b>			
Levigated Kaolin from Zettlitz in Bohemia .	$12.82(Al_2O_3 \cdot 1.35SiO_2) + RO$	70—60	$\frac{12.82}{1.35} = 9.49$
<b>CLASS III.</b>			
a. Crude Kaolin from Saarau . . . . .	$14.15(Al_2O_3 \cdot 5.01SiO_2) + RO$	50	$\frac{14.15}{5.01} = 2.82$
b. Belgium clay, from Strudmolsereul, near Ardennes . . . . .	$6.86(Al_2O_3 \cdot 1.63SiO_2) + RO$	50	$\frac{6.86}{1.63} = 4.21$
<b>CLASS IV.</b>			
Clay from Mühlheim, near Coblenz; best average sample . .	$5.96(Al_2O_3 \cdot 1.51SiO_2) + RO$	45	$\frac{5.96}{1.51} = 3.95$
<b>CLASS V.</b>			
Clay from Grünstadt, in the Pfalz . . . . .	$3.65(Al_2O_3 \cdot 1.54SiO_2) + RO$	30	$\frac{3.65}{1.54} = 2.37$
<b>CLASS VI.</b>			
Clay from Mönchsberg, near Cassel . . . . .	$4.41(Al_2O_3 \cdot 2.37SiO_2) + RO$	20	$\frac{4.41}{2.37} = 1.86$
<b>CLASS VII.</b>			
Clay from Niederpleis, on the Sieg . . . . .	$3.89(Al_2O_3 \cdot 2.37SiO_2) + RO$	10	$\frac{3.89}{2.37} = 1.64$

A comparison of these numbers leads to the following results:—1. The quotients in the fourth column decrease in the same order as the numbers in the third, which express the fire-resisting powers directly determined; and in the most refractory clays the differences of the quotients are large for small differences in the fire-resisting powers.

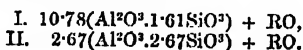
2. The crude Kaolin of Saarau, in Class III., forms a striking exception to this rule. Direct experiments showed, however, that this Saarau clay, when ground to an impalpable powder, is more fusible than the Mühlheim clay in Class IV., and appears more refractory in its crude state merely because it contains coarse grains of quartz.

3. It is remarkable, also, that the average sample of Saarau clay (Class I.) and the clay from Zettlitz (Class II.) give quotients so nearly equal, although they differ considerably in their fire-resisting power. But in this case, also, the peculiarity is due to the state of aggregation, the Zettlitz kaolin being in the state of an extremely soft powder, which yields to the softening influences of a high temperature more readily than the compact stony clay of Saarau.

In the preceding considerations no account has been taken of the proportions between the silica and the fluxes; and, indeed, Bischof shows that this proportion does not afford a satisfactory criterion of the pyrometric value of a clay. In the coal-formation of Saarbrück there are found, in the Wellesweiler and Duttweiler pits, two clays, belonging unmistakably to the same species, and having the character of slate-clays, but differing considerably in their degree of purity: the Wellesweiler clay being comparatively pure, whereas that from Duttweiler is more contaminated with sand, and especially with iron-oxide and magnesia. Their composition is given in the following table, I. denoting the clay from Wellesweiler, II. that from Duttweiler:—

	SiO <sup>2</sup> and Sand	Al <sup>2</sup> O <sup>3</sup>	FeO	CaO	MgO	K <sup>2</sup> O	Loss on ignition	
I. {	38.05	35.19	.28	.45	.31	1.13	13.70	= 100.61
	11.50							
II. {	29.35	25.13	1.95	.50	1.49	1.70	10.90	= 100.27
	29.25							

From which may be calculated the formulæ—



representing the following proportions:—

	I.	II.
Alumina to fluxes . . .	10.78 : 1	2.67 : 1
Alumina to silica . . .	1 : 1.61	1 : 2.67
Quotient . . . . .	$\frac{10.78}{1.61} = 6.70$	$\frac{2.67}{2.67} = 1$
Silica to fluxes . . . .	17.36 : 1	7.13 : 1

Here, then, we see that although the ratio of silica to fluxes is much greater in I. than in II., the quotient  $\frac{A}{B}$  is also greater: hence the greater fire-resisting power of the first variety.

In the two clays from Saarau (Class I.) the ratio of fluxes to silica is, in the refractory, as 1 : 27.70; in the more refractory, as 1 : 26.57. Lastly, in two clays from Namur, having respectively the formula  $12.28(\text{Al}^2\text{O}^3.2.25\text{SiO}^2) + \text{RO}$  and  $7.18(\text{Al}^2\text{O}^3.2.51\text{SiO}^2) + \text{RO}$ , and giving for the first the quotient  $\frac{A}{B} = 5.46$ , for the second 2.86, the ratio of fluxes to silica is, in the first, which is the more refractory, 1 : 27.83, in the second, or more fusible, 1 : 18.02.

Whereas, then, in the clays from Saarbrück and from Namur, the ratio of silica to fluxes increases with the fire-resisting power, the contrary holds good in the clay from Saarau, the more refractory clay from this locality containing less silica in proportion to the fluxes than the less refractory.

These considerations show that though the determination of the quantities of silica

and fluxes contained in a clay is of this great importance for the determination of its fire-resisting power, the ratio of the silica to the fluxes does not of itself afford any safe criterion for that determination. Fire-clays, in fact, are double compounds, which cannot be correctly compared by a one-sided consideration of the ratio of silica to fluxes without regard to the alumina. This, indeed, Bischof has clearly shown by experiments on the fusibility of mixtures containing 100 parts of silica to 1, 2, and 4 parts of alumina, and 100 parts silica to 1, 2, and 4 parts of magnesia. The most fusible of these mixtures is that which contains 4 parts alumina to 100 silica. In presence of so large a proportion of silica, alumina is a better flux than magnesia. Independently, also, of the uncertainty attending the valuation of a fire-clay solely by reference to the ratio of silica to fluxes, the consideration of this ratio is, in fact, superfluous, the ratio of the aluminium silicate to the fluxes and of the alumina to the silica being quite sufficient to afford a trustworthy estimate of the pyrometric value of a clay. It is, of course, understood, that the analytical determinations must be made with all attainable exactness.

The following analyses of fire-clays are also by Bischof (*Diagl. polyt. J. cxxxiii. 29; cxxxv. 39; Jahresb. 1867, 920*): *a.* From Ebernheim near Vallendar, on the Rhine. *b.* From Mühlheim on the Rhine. *c.* From Grünstadt in the Bavarian Palatinate. The clays were analysed after drying at 100°.

	<i>a</i>	<i>b</i>	<i>c</i>
Al <sub>2</sub> O <sub>3</sub> . . . . .	37.95	35.36	35.05
SiO <sub>2</sub> combined . . . . .	32.18	35.35*	39.32*
SiO <sub>2</sub> as sand . . . . .	14.79	12.41	8.31
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.95	2.69†	2.30
CaO . . . . .	0.04	0.16	0.16
K <sub>2</sub> O . . . . .	3.00	1.24	3.18
MgO . . . . .	0.11	0.07	1.11
Loss by ignition ‡ . . . . .	12.02	11.72	10.51
	101.04	99.00	99.64

\* With traces of titanio acid. † Partly as FeO. ‡ Water and organic matter. The amount of water in the air-dried state is in *a* 8.75 p.c.; in *b* 13 p.c.; and in *c* 5.8 p.c.; *b* contains traces, *c* 0.084 p.c. sulphur (as pyrites).

Goppelsröder (*J. pr. Chem. ci. 444; Jahresb. 1867, 1030*) has analysed clays used for making fire-bricks found at Hofstetten and Witterschweiler in the neighbourhood of Basel; A and B light greyish-yellow to yellow, white in parts, with veins having the colour of iron rust; C greyish-white to yellow with the same veins.

SiO <sub>2</sub> and Sand	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Water and Organic Matter
76.919	11.358	3.084	1.793	0.481	2.248		4.117
78.911	7.171	3.031	1.991	0.272	1.413	0.620	6.590
53.425	92.730	6.378	4.990	0.530	1.355	0.872	9.920

The following analyses of various kinds of clay are by K. von Hauer (*Jahrb. geolog. Reichsanstalt, xix. 428, 430, 432; Jahresb. 1869, 1076*): 1. Kaolin from Budweis; 2. Fire-clay from Rév in Hungary; 3. Fire-clay from Oberfucha in Lower Austria; 4. Porcelain-clay from Mahrenberg on the Drau:—

	1.	2.	3.	4.
SiO <sub>2</sub> . . . . .	48.6	60.3	67.0	Aluminium silicate . . . . . 87.6
Al <sub>2</sub> O <sub>3</sub> . . . . .	43.0	28.0	20.6	Soluble alumina . . . . . 6.6
Fe <sub>2</sub> O <sub>3</sub> . . . . .	—	—	—	Ferric oxide . . . . . trace
MgO . . . . .	trace	—	—	Magnesia . . . . . 2.1
CaO . . . . .	—	0.5	0.2	Water . . . . . 4.6
Water . . . . .	8.2	10.6	11.3	
	99.8	99.3	99.1	99.8

**COAL.** *Estimation of Sulphur in Coal and Coke.*—The method usually adopted for the estimation of sulphur in coal and coke, consists in treating a known weight of the finely powdered material with nitromuriatic acid, and after digesting it at a moderate temperature until the whole of the sulphur is supposed to be converted into sulphuric acid, determining the latter as barium sulphate.

In operating in this manner there are several sources of error. In the first place, the figures obtained include the sulphur or sulphuric acid combined with calcium, as well as that existing as pyrites in the coal; and it is obviously most important, with regard to the use of coal in iron-smelting, that those figures should be returned separately, since the sulphur, combined with the calcium as sulphate or sulphide, is perfectly harmless, while the pyrites seriously affect the quality of the iron, by combining with it as ferrous sulphide during the process of smelting.

Again, in carrying out the above-mentioned process, unless the nitric acid be carefully and entirely removed by evaporation, grave errors in the weight of barium sulphate will ensue, and if the evaporation of the nitromuriatic acid be carried too far, a basic iron sulphate is sometimes formed, which even long boiling with water fails to remove from the carbonaceous mass, so that a deficiency of sulphur is entailed.

To remedy these defects, Calvert (*Chem. News*, xxiv. 76) operates in the following manner:—A weighed portion of the finely powdered coal is boiled in water with an equal weight of sodium carbonate for twenty hours, by which means the calcium sulphate is decomposed, while the iron sulphide remains unattacked. The residue is then filtered, and rapidly washed with boiling water. In the case of coke, nitric acid in slight excess must be added to the filtrate, to convert the sodium sulphide into sulphate, and the sulphuric acid therein determined in the usual manner. The sulphur found in the residue will then correctly represent the amount of pyrites present in the coal.

In estimating this latter, Calvert objects to the dry oxidising process, since it invariably entails a slight loss of sulphur. A more exact method is to oxidise with nitromuriatic acid, then concentrate the liquid, add sodium carbonate in excess, and heat the whole to near the fusing point, by which means the iron, silica, and alumina, are rendered insoluble. The mass is then treated with water, well washed, and the filtrate acidified with acetic acid; barium chloride will now precipitate the whole of the sulphuric acid from this solution.

The figures in the subjoined table contrast the results obtained from three distinct samples, when analysed by the old and by the improved method:

	Old process		New process		In washings		Difference
	Sulphur p.c.	Mean	Sulphur p.c.	Mean	Sulphur p.c.	Mean	
1. . . . .	{ 1.36 1.40	1.38	{ 0.60 0.58	0.59	{ 0.79 0.78	0.79	0.79
2. . . . .	{ 1.59 1.55	1.57	{ 0.63 0.67	0.65	{ 0.97 0.95	0.96	0.92
3. . . . .	{ 1.78 1.73	1.75	{ 0.89 0.85	0.87	{ 0.85 0.88	0.87	0.88

The relative proportions of iron and sulphur in the pyrites of Iowa coal have been determined by R. Emery (*Sill. Am. J.* [3] iii. 34). The coal was first treated with very dilute hydrochloric acid, so as to remove everything which was soluble in that menstruum. The residue was then oxidised with hydrochloric acid and potassium chlorate, and the percentage of iron and sulphur calculated in the usual manner.

Ten samples were examined. In four samples the relative proportions of iron and sulphur corresponded very closely with that existing in  $\text{FeS}_2$ , viz., 53.3 p.c. of sulphur. In four samples there was a decided excess of sulphur, the percentage rising in two instances to 63.0 p.c., while in two samples there was a marked deficiency of sulphur, 45.0 and 50.0 p.c. only being found.

The results of the analyses of the coals of Ohio, by Prof. Wormley, show that in every instance the amount of sulphur present is too large for combination with the iron as bisulphide.

**Gases enclosed in Coal.** E. v. Meyer has examined the gases enclosed in coal from several coal-fields in Germany (*J. pr. Chem.* [2] v. 144, 418; vi. 389), and in English coal from the Newcastle and Durham districts (*ibid.* v. 407).

The gases were obtained by introducing two to four hundred grams of the coal into a flask, which was immediately filled up with hot de-aerated water, and the water was boiled so as to expel the gases from the coal, and drive them through a short straight tube fitted by a caoutchouc plug to the mouth of the flask into a number of tubes inserted in a basin of water supported on the end of the tube proceeding from the flask. The gases so collected were analysed by Bunsen's method.

Coals from several districts were examined, both when freshly raised, and after having been exposed to the influence of the weather for times varying from one to several years.

The majority of coals gave by this treatment gases agreeing in composition with those known to occur in ordinary mine gas, that is, carbon dioxide, oxygen, nitrogen, and marsh-gas.

The quantity of gas contained in various coals freshly raised and long weathered, is shown by the following table (Mem., the indication numbers attached to the name of the coal will be retained throughout the article to indicate the same sample):—

	100 grams of	
	Freshly raised	Weathered
(1). Zwickau coal gave . . . . .	38.0 c.c.	(a) 18.0 c.c.
(2). " " " " . . . . .	25.5 "	(a) 18.6 "
(3). " " " " . . . . .	54.8 "	(a) 13.6 "
(4). Westphalian, from Essen . . . . .	22.5 "	
(5). " " Bochum . . . . .	50.6 "	(a) 43.2 "
(6). " " " " . . . . .	50.4 "	(a) 39.2 "

The composition of these gases presents peculiarities in two cases only, viz., 1 (a) and 3 (a), which, it is to be observed, are both from coals altered by weathering.

The composition of the gases from fresh coal is shown by the following table:

	CO <sup>2</sup>	O	N	CH <sup>4</sup>
1 . . . . .	2.42	2.51	23.17	71.0
2 . . . . .	4.02	0.62	50.36	45.00
2 (a) . . . . .	2.25	0.7	23.89	73.16
3 . . . . .	0.6	trace	48.0	51.4
4 . . . . .	7.5	2.59	89.91	—
5 . . . . .	4.87	2.66	75.82	16.65
5 (a) . . . . .	11.12	2.88	78.6	7.4
6 . . . . .	1.30	1.60	66.85	30.25
6 (a) . . . . .	4.35	3.35	81.18	11.12

These numbers selected from those given show that exposure to the weather causes a loss of a great part of the marsh-gas, as was to be expected, but the ratio of oxygen to nitrogen and carbon dioxide also serves to show that in the process of the passage of vegetable remains into coal, the oxygen of the air concerned has gone mostly to the burning of the hydrogen, leaving the carbon comparatively intact.

The gas obtained from 1 (a) and 3 (a) was quite different in composition from that obtained from any other specimen:—

	CO <sup>2</sup>	O	N	CO	OH <sup>2</sup>	C <sup>2</sup> H <sup>4</sup>	Absorbed by fuming sulphuric acid
1 (a) . . . . .	16.7	4.9	55.15	—	3.17	18.61	1.47
Ditto, collected one week later . . . . .	11.4	3.8	60.08	—	3.44	18.88	1.5
Ditto, collected two weeks later than the preceding . . . . .	12.10	1.10	65.16	—	3.19	16.85	1.6
3 (a) . . . . .	7.62	2.44	50.75	—	15.88	22.35	0.96
Ditto, collected one week later . . . . .	10.10	2.6	50.53	1.82	10.18	23.32	1.45
Ditto, collected two months later than the preceding . . . . .	11.18	2.82	07.99	—	—	10.86	1.65

The analytical data obtained (oxygen consumed, contraction, and carbonic acid formed) seem to leave no doubt that ethane was really a constituent of the gas obtained from these coals.

Three specimens of grey shaley coal containing much pyrites, gave gases characterised by the absence of hydrocarbons, and the preponderance of carbon dioxide. As it is well known that coals which contain much pyrites, oxidise more readily than others, the formation of the product of the combustion of carbon can be explained in this case by the greater energy of the oxidising action. The gases in this case had the following composition:—

	CO	O	N
7 . . . . .	48.7	1.8	49.5
8 . . . . .	38.2	1.2	60.6
9 . . . . .	54.9	1.2	43.9

Further experiments were made to determine whether exposure of a coal to a continued temperature of 50° caused an alteration resulting in further production of gas, or if the gases contained in it underwent any change of composition. The Zwickau coal, 1 (a), after the last of the analyses above quoted, was left between three and four months in a cool dry place, when it was found to give off gas of the composition—

CO<sup>2</sup> = 12.91, O = 2.57, N = 57.8, C<sup>2</sup>H<sup>4</sup> = 22.62, CH<sup>4</sup> = 4.06 per cent.

At the time that this examination was made, another portion of the coal was kept for two days at 45°, and then immediately treated in the usual manner, when it evolved gas as rapidly as the unwarmed portion. It was found to be free from marsh-gas. The composition of the gas was:—

CO<sup>2</sup> = 10.65, O = 3.2, N = 74.72, C<sup>2</sup>H<sup>4</sup> = 9.8, and gas absorbed by sulphuric acid, 1.63 per cent.

By calculation it is shown that the heavy hydrocarbon is probably butylene.

It thus appears that on warming, the whole of the marsh-gas escapes first, by reason of its greater diffusibility.

The gases from another coal from Zwickau were also examined both before and after heating the coal to 50° for twenty-four hours. The hydrocarbons present were methane, ethane, and butylene. In the gas from the heated coal, some higher term of the paraffin series, probably propane, appeared to be present. The analytical numbers agree well with those required by:—

CO<sup>2</sup> = 15.6, O = 3.10, N = 73.33, C<sup>2</sup>H<sup>4</sup> = 4.39, C<sup>2</sup>H<sup>2</sup> = 2.06, C<sup>2</sup>H<sup>6</sup> = 1.75.

Coal from the Saar district yielded gases containing, besides methane, some of its homologues, which were calculated as C<sup>2</sup>H<sup>6</sup>. Ethene, which G. Bischof found, Meyer was unable to detect. The coal from the Gerhard pit is as hard and dense as Durham coal, and the gases contained in it resemble in quality and quantity those enclosed in the latter. The following table contains the results:—

Locality and time when the coal was examined	CO <sup>2</sup>	CH <sup>4</sup>	C <sup>2</sup> H <sup>4</sup>	O	N	100 grams gave a.c. gas
<i>Kronprinz Pit.</i>						
(A.) <i>Wahlshied Seam.</i>						
Glass blown out of a fissure (mixed with air) . . . . .	0	23.57	—	16.09	60.34	—
Air from the pit (where coal had just been removed) . . . . .	1.25	2.39	—	17.77	78.59	—
2 weeks . . . . .	4.05	2.65	—	16.17	78.13	—
10 weeks . . . . .	8.51	63.86	3.88	0.25	23.50	—
2 weeks . . . . .	33.66	24.08	4.72	0.81	36.73	42.0
2 weeks . . . . .	4.85	72.88	—	0.0	22.27	—
(B.) <i>Schwalbach Seam.</i>						
3 weeks . . . . .	4.57	51.81	—	0.26	37.41	—
5—6 weeks . . . . .	49.95	15.04	—	1.39	33.62	32.0
3—4 weeks . . . . .	30.05	16.06	13.36	1.16	32.40	19.0
5 weeks . . . . .	29.50	12.44	9.48	3.09	45.49	25.0
4 weeks . . . . .	15.22	52.12	—	0.66	32.10	32.5
<i>Geislautern Pit.</i>						
No. 4 seam, 6 weeks . . . . .	19.19	37.94	3.22	0.97	38.68	35.0
No. 6 seam, 8 weeks . . . . .	35.66	9.46	3.61	2.63	48.64	21.5
No. 6 seam, 6 weeks . . . . .	26.12	55.65	—	1.20	17.08	68.0
<i>Gerhard Pit.</i>						
Fire-damp . . . . .	0.62	22.52	—	14.01	62.85	—
Anna seam . . . . .	—	91.76	—	—	8.24	15.0
Sophie seam . . . . .	1.83	90.79	—	—	7.38	15.0
Max seam . . . . .	2.90	89.93	—	—	7.27	15.0



*Gases enclosed in English Coal.*—The following are the results of the examination of the gases obtained from eight samples of coal from the Newcastle and Durham districts:—

- No. 1. Low Main seam, from Bewicke Main Colliery (Newcastle district).  
 No. 2. Maudlin seam, from Bewicke Main Colliery (Newcastle district).  
 No. 3. Main coal seam, Urpeth Colliery, Newcastle (Durham district).  
 No. 4. 5-seam, Urpeth Colliery, 30 fathoms from surface.  
 No. 5. 5-seam, Wingate Grange Colliery, Durham district, 74 fathoms from surface.  
 No. 6. Low main seam, Wingate Grange Colliery, 108 fathoms from surface.  
 No. 7. Harvey seam, Wingate Grange Colliery, 148 fathoms from surface.  
 No. 8. Harvey seam, Emily Vil., Woodhouse Close Colliery, 25 fathoms from surface; district not given.

From the following table it will be seen that no other hydrocarbon than marsh-gas was found in any case:—

No. of Analysis	District	CO <sup>2</sup>	CH <sup>4</sup>	O	N	100 grm. gave — c. c. gas
1	Newcastle	5.55	6.52	2.2	85.65	25.2
2	"	8.54	26.54	2.95	61.97	30.7
3	Newcastle—Durham.	20.86	—	4.83	74.31	27.4
4	"	16.51	trace	5.65	77.84	24.4
5	Durham	0.34	85.8	trace	13.86	91.2
6	"	1.15	84.04	0.19	14.62	238.0
7	"	0.23	89.61	0.55	9.61	211.2
8	Unknown	5.31	50.01	0.63	44.05	84.0

Taking the specific gravity of coal as 1.3, it will be seen that Nos. 6 and 7 contain nearly three times their volumes of gases measured at ordinary pressures, and that therefore, as the coal is very hard and dense, the condensation of that gas must be very great.

*Gases enclosed in certain Lignites.*—(Kolbe u. Zitowitsch, *J. pr. Chem.* [2] vi. 79). The gas which accumulates in lignite mines has long been recognised and dreaded as consisting mainly of carbon dioxide, whereas marsh-gas has never been detected in it. The great oxidability of lignite has been demonstrated by the experiments of Varrentrapp (*Chem. Centr.*, 1865, p. 953).

The gases enclosed in Bohemian patent lignite, and in an earthy lignite of inferior quality, have been examined by Zitowitsch. The mode of collection was the same as that adopted by v. Meyer with pit-coal. The quantity obtained from both varieties was small, and was not determined. The gases were found to consist of carbonic anhydride, carbon monoxide, nitrogen and oxygen, in the following proportions:—

Gas from	CO <sup>2</sup>	CO	N	O
I. } Bohemian lignite	80.60	1.80	8.03	0.51
II. }	82.40	3.00	14.15	0.45
III. Earthy lignite	83.99	1.04	14.91	0.65

**Coal Tar and Pitch.** The composition of coal-tar varies considerably with the temperature at which coal is distilled; the higher the temperature the larger is the yield of solid bodies. Tar produced in gas-retorts contains more benzene and toluene, but also more naphthalene and other solid hydrocarbons than that obtained by distilling coal in coke-furnaces in which the distillation takes place at a lower temperature; the latter tar contains chiefly liquid hydrocarbons and a considerable quantity of compounds soluble in alkalis, but only a very small quantity of carbonic acid. When heavy coal-tar oil is allowed to run into a furnace heated to a bright-red heat, it yields, besides naphthalene, 2 per cent. of benzene and toluene and a little xylene, but only traces of higher homologues. At a lower temperature the decomposition of the oil is less complete, and at a higher temperature, the benzene is converted into naphthalene. In the furnaces there remains a kind of graphite, which is a very valuable fuel for producing high temperatures.

The pitch which is left behind in the distillation of tar is partially soluble in benzene and carbon sulphide; the residue consists of a black powder having the composition of Welsh anthracite. When pitch is passed through a red-hot tube, it yields about 250 vol. of a gas consisting almost entirely of hydrogen; but on distilling it from a retort, it yields about 25-30 per cent. of an oil containing pyrene, chrysene, and anthracene. The other products consist of 0.2 per cent. of light oils and gases containing ammonia and hydrogen, and 48-52 per cent. of coke is left behind. In some works the pitch is distilled with over-heated steam in order to obtain anthracene; in this case the residue is a very brittle pitch, which is mixed with naphthalene, and then used like the undistilled pitch, as asphalt, or as fuel, by mixing it with coal-dust and forming the mass into bricks, and for other purposes (Behrens, *J. pr. Chem.* [2] vi. 277).

**COBALT.** Co.—*Atomic Weight.*—R. II. Lee (*Sill. Amer. J.* [3] ii. 44) has determined the atomic weight of this metal by the analysis of crystalline cobaltcyanides of alkaloids having high atomic weight.

Commercial cobaltic oxide was first converted into an impure sulphate, and the solution of the salt treated with a current of hydrogen sulphide to remove all metals precipitable by that gas. The iron in the filtrate was peroxidised with chlorine, and afterwards removed, together with manganese, by the addition of barium carbonate. The solution was then treated with a large excess of barium carbonate, and gaseous hydrogen cyanide passed into the liquid, until the whole of the cobalt was converted into cobalticyanide of barium. The nickel, as well as traces of iron and manganese, still present in the solution, were removed by boiling with mercuric oxide, and the mercury having been removed from the filtrate by hydrogen sulphide, the solution of barium cobalticyanide was regarded as chemically pure.

The brucine and strychnine salts were prepared by decomposing the sulphates of these bases with the above solution of cobalticyanide, and repeatedly crystallising the salts formed. The crystals of the two alkaloids closely resemble each other; they are but slightly soluble in water, crystallising almost completely from their solutions on cooling. The water of crystallisation having been directly determined, the quantity of cobalt was found by carefully burning the salt in a platinum crucible, first in air, then in oxygen, and finally reducing the oxide to the metallic state by a current of pure hydrogen.

The atomic weight of the metal, calculated from the mean results of six analyses of the strychnine salt, was fixed at 59.05, and from a similar number of analyses of the brucine salt, at 59.15. As a check upon the foregoing numbers, another series of experiments was made by igniting the chloride of purplecobalt in a current of hydrogen. The atomic weight calculated from the per-centage of metal obtained was found to be 59.09.

The mean of all these determinations, eighteen in number, is 59.10: a result higher than those obtained by all other experimenters, except Schneider (60) and Sommaruga (59.93); almost identical with that of Dumas (59.08); differing somewhat more from that of Rothoff, and from the higher number given by Marignac (59.02), still more from Marignac's lower number (58.64), and from those of Winkler (58.92) and Russell (58.74).

*Physical Properties.*—According to Valenciennes (*Compt. rend.* lxx. 607) cobalt, after fusion and rolling, has the aspect of polished iron: it is harder, but may be rolled into spiral bands like good iron.

Respecting alloys of cobalt and copper, see COPPER.

On the coating of metals with Cobalt and Nickel, see Stolba (*Dingl. pol. J.* ccl. 145).

*Detection, and Distinction from Nickel, Manganese, and Zinc.*  
*a. By Sodium Sulphocyanate.*—On adding a drop of a concentrated solution of cobalt to strong solution of sodium sulphocyanate, a blue coloration is produced, owing to the formation of a compound which crystallises, either at once or after spontaneous evaporation, in long blue needles insoluble in carbon bisulphide. When the cobalt solution is dilute, the colour appears only on warming. It is advisable to evaporate the cobalt solution nearly to dryness, add the sulphocyanate, and warm. In this way cobalt may be detected in one drop of a solution containing 0.0005 grm. in 1 c.c. Iron, nickel, zinc, and manganese do not interfere with the reaction, provided the solutions are neutral (Schönn, *Zeitschr. anal. Chem.* 1870, 209).

*b. By Potassium Ferricyanide.*—When a solution of a cobalt salt is mixed with ammoniac, ammonia, and excess of potassium ferricyanide, the liquid immediately assumes a deep blood-red coloration, similar in appearance to the reaction between potassium sulphocyanate and a ferric salt: the solution remains perfectly clear even on heating, and no precipitation whatever of the cobalt takes place.

When a salt of nickel is similarly treated, and the solution gently boiled, the liquid first becomes turbid, and in a short time deposits the whole of the nickel as a copper-red precipitate, which has a great tendency to adhere to the sides of the vessel. The presence of cobalt in no way interferes with the precipitation of the nickel, neither does this latter metal obscure the coloration produced by the cobalt: the foregoing test affords therefore a ready means of detecting these two metals when they occur together in the same solution.

When a solution of manganous sulphate is treated with ammonium chloride and ammonia, and potassium ferrieyanide gradually added, a whitish precipitate is formed, which changes, with the addition of more ferrieyanide, to a dark brown colour. As this reaction takes place immediately in the cold, it may serve to distinguish manganese from cobalt and nickel; the manganese, however, interferes with the subsequent tests for cobalt and nickel, when all three metals are present in the same solution.

An ammoniacal solution of zinc sulphate, in presence of ammonium chloride, is not precipitated, either in the cold or on boiling, by the addition of potassium ferrieyanide; but potassium ferrocyanide instantly throws down the zinc as a white precipitate.

Since the four metals, nickel, cobalt, manganese, and zinc, frequently occur in analysis in presence of ammoniacal salts, the above method may be useful as an additional mode of distinguishing between them. The characteristic reactions are:

1. A brown precipitate indicates manganese.
2. A deep red solution indicates cobalt.
3. No change in the cold, but a copper-red precipitate on boiling indicates nickel.
4. No change in either hot or cold liquid; a white precipitate on addition of potassium ferrocyanide indicates zinc (Allen, *Chem. News*, xxiii. 290).

**Bromide,  $\text{CoBr}^2$ .** When metallic cobalt is left for about a week in contact with bromine and a little water, and the filtered purple solution is then evaporated, it assumes a splendid blue colour, and on evaporation over sulphuric acid, deposits purple-red prismatic crystals of the hexhydrate  $\text{CoBr}^2 + 6\text{H}_2\text{O}$ . This hydrate is both deliquescent and efflorescent; when heated to  $100^\circ$  it melts and gives off two-thirds of its water, leaving the dihydrate  $\text{CoBr}^2 + 2\text{H}_2\text{O}$ , which, on cooling, forms a mass of purplish-blue crystals covered with a blue opaque crust. This hydrate, which is deliquescent, gives off the whole of its water at  $130^\circ$ , leaving the anhydrous bromide in the form of a vivid green, deliquescent, amorphous mass (W. N. Hartley, *Paper read before the Chemical Society*, April 2, 1874).

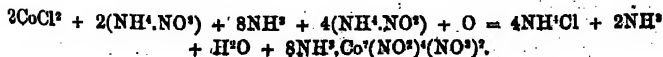
**Iodide,  $\text{CoI}^2$ .** Cobalt, treated with iodine and water, yields a red liquid which, when evaporated down till it turns green, and then placed over sulphuric acid, assumes a brown colour on cooling down to  $16^\circ$ , and after a day or two deposits the hexhydrate  $\text{CoI}^2 + 6\text{H}_2\text{O}$  in large deliquescent hexagonal prisms having the colour of dark smoky quartz. When the red solution is evaporated down till a steam forms on the surface, and then left over sulphuric acid, it yields a compact mass of green deliquescent crystals consisting of the dihydrate  $\text{CoI}^2 + 2\text{H}_2\text{O}$ . This hydrate, on exposure to the air, deliquesces first to a green, then to a brown, and finally to a red solution. By heating either of these hydrates to  $130^\circ$ , the anhydrous iodide is obtained as a black mass, having a graphitic lustre (Hartley).

#### COBALT-BASES, AMMONIACAL (i. 1051; 1st Suppl. 477).

**Dinitro-octammoniocobaltic or Croceocobaltic salts,  $8\text{NH}_4^+\text{Co}^2(\text{NO}_2)^2\text{X}^2$**  (Gibbs, *Sill. Am. J.* [3] vi. 116).—These salts are formed, like the xanthocobaltic salts, by the action of alkaline nitrites on ammoniacal solutions of cobalt, the production of a salt of one or the other series depending upon the conditions of the experiment.

The croceocobaltic salts resemble those of xanthocobalt; they have a fine sherry-wine colour, and are but sparingly soluble even in boiling water. They nevertheless crystallise well. The solutions are decomposed by boiling, with evolution of ammonia, but the addition of a small quantity of acetic acid prevents or retards the decomposition.

The nitrate  $8\text{NH}_4^+\text{Co}^2(\text{NO}_2)^2(\text{NO}_3)^2$  is prepared by mixing a solution of cobaltous chloride with ammonium nitrate, and then with ammonium nitrate containing much free ammonia; the solution absorbs oxygen, acquires a deep orange colour, and after some time deposits the nitrate abundantly in orange-brown crystals. The reaction is:—



If potassium nitrite and cobaltous nitrate are used in this reaction instead of ammonium nitrite and cobaltous chloride, a similar orange-yellow crystallisation is obtained, which, however, on recrystallisation, separates into prismatic crystals of croceocobaltic nitrate and octahedral crystals of xanthocobaltic nitrate.

Croceocobaltic nitrate is most easily obtained in the pure state by boiling the sulphate with barium chloride and a little acetic acid. It crystallises in orange-yellow needles or prisms, slightly soluble in cold water, more soluble in boiling water and in dilute acid. It explodes when heated, though not violently. It is distinguished from xanthocobaltic nitrate by its crystalline form, and by yielding a splendid cinnabar-red precipitate with a solution of iodine in potassium iodide, and a precipitate of orange-yellow needles with potassium dichromate.

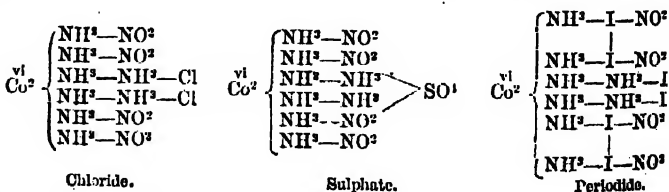
The sulphate  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{SO}_4$  is obtained by treating a solution of cobaltous sulphate with ammonia and potassium nitrite. The solution, on exposure to the air, gradually deposits orange-yellow crystals and a green flaky substance. On filtering, a bright green mass of cobaltic hydrate, mixed with orange-yellow crystals, remains in the filter, and the solution of this mass in boiling in very dilute sulphuric acid deposits the sulphate in crystals on cooling. From hot concentrated solutions the sulphate is deposited in small very brilliant yellow scales which, under the microscope, appear to belong to the quadratic system. In larger crystals it has a dark wine-red colour like that of xanthocobaltic salts. It is but slightly soluble in water, even at the boiling heat, more soluble in hot dilute sulphuric acid.

The chloride  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{Cl}_2$  is best prepared by boiling the crude sulphate with barium chloride, and a little hydrochloric acid. It forms beautiful iridescent crystals of the characteristic sherry-wine colour, which are rather more soluble than those of the sulphate. It combines with various metallic chlorides, forming double salts. The *aurichloride*,  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{Cl}_2 \cdot 2\text{AuCl}_3$ , forms an indistinctly crystalline precipitate of a fine canary-yellow colour. The *platino-chloride*,  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{Cl}_2 \cdot \text{PtCl}_4$ , separates in fine orange-brown prismatic crystals on adding a solution of sodium-platinic chloride to croceocobaltic nitrate.

The *chromate*,  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{CrO}_4$ , and *dichromate*,  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{Cr}_2\text{O}_7$ , are obtained by precipitating a solution of the nitrate with potassium monochromate or dichromate; the first forms brilliant lemon-yellow scales, the second orange-yellow needles.

The *periodide*,  $8\text{NH}_3 \cdot \text{Co}^2(\text{NO}^2)_2 \cdot \text{I}_2$ , is obtained as a crystalline precipitate of a magnificent cinnabar-red colour on adding a solution of iodine in potassium iodide to a solution of the nitrate. Heated with a solution of sodium sulphite it is immediately converted into the yellow di-iodide.

The chloride sulphate and periodide of this series may be represented by the following constitutional formulæ, 4 of the iodine-atoms in the last being regarded as trivalent:—



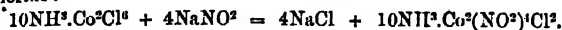
*Erdmann's salt*.—When potassium nitrite is added to a solution of cobaltous chloride-containing excess of ammonium chloride, oblique rhombic crystals are deposited, to which Erdmann assigned the formula  $\text{Co}^2(\text{NH}_3)_4(\text{NO}^2)_2 \cdot \text{K}^2$  (*1st Suppl.* 870). This salt exhibits a curious relation to the croceocobaltic salts, the number of atoms of  $\text{NO}^2$  in either of the two being the same as that of the atoms of  $\text{NH}^2$  in the other. Further, on adding a solution of Erdmann's salt to a solution of croceocobaltic nitrate, potassium nitrate is formed, and a double nitrite,  $\text{Co}^2(\text{NH}_3)_4(\text{NO}^2)_2 \cdot \text{Co}^2(\text{NH}_3)_4(\text{NO}^2)_2$ , is precipitated, which gives the reactions of the croceocobaltic salts.

A few other octammoniated cobaltic salts have been described by various chemists. Gibbs and Gent, in 1856, obtained, in more than one reaction, small quantities of a leak-green crystalline precipitate, the base of which they termed provisionally *præcocobalt*. This body was afterwards described by F. Ross, according to whose analyses its composition is  $\text{Co}^2(\text{NH}_3)_4 \cdot \text{Cl}_4$ . Künzel (*J. pr. Chem.* lxxii. 218) obtained a hypsulphate which appeared to have the composition  $\text{Co}^2(\text{NH}_3)_4 \cdot \text{S}_2\text{O}_8$ .

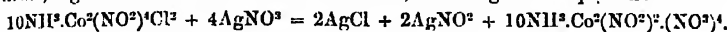
*Flavocobaltic salts* (Gibbs, *Deut. Chem. Ges. Ber.* iii. 42).—These octammoniated compounds are closely related to the xanthocobaltic salts; e.g.:



*Flavocobaltic chloride* is obtained by adding a hot solution of *purpureocobaltic chloride* to a solution of sodium nitrite mixed with a few drops of acetic acid; the liquid then acquires a deep orange colour, and, on cooling, deposits crystals of *flavocobaltic chloride*:



*Flavocobaltic chloride* is very much like *xanthocobaltic chloride*, and forms well-crystallised double salts with the chlorides of gold, platinum, tin, mercury, and other metals. Treated with an acid solution of silver nitrate, it yields *xanthocobaltic nitrate*, together with silver chloride and nitrite, according to the equation:

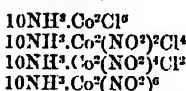


With ammonium oxalate it yields *xanthocobaltic oxalate*, together with ammonium chloride and nitrite. With potassium ferrocyanide, it yields *xanthocobaltic ferrocyanide*:



*Flavocobaltic sulphate* has the composition  $10\text{NH}_3\cdot\text{Co}^2(\text{NO}_2)^2\cdot\text{SO}_4^4$ ; the *nitrate* is anhydrous and contains  $10\text{NH}_3\cdot\text{Co}^2(\text{NO}_2)^4(\text{NO}_2)^2$ . The chloride, sulphate and nitrate, are crystalline, have a deep orange-red colour, and are easily soluble in hot water; they give flocculent precipitates with cyanides of alkali-metal, and with the nitrates of platinum, cobalt, nickel and cadmium; *xanthocobaltic nitrate* does not form a precipitate with either of these reagents.

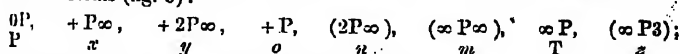
*Purpureocobaltic chloride* forms, with silver nitrate, a brown-orange-coloured solution which, after evaporation, deposits octahedral crystals of the salt  $10\text{NH}_3\cdot\text{Co}^2(\text{NO}_2)^4$ . We have, then, the following series of salts:—



Some *roseocobaltic* and *purpureocobaltic salts* are capable of taking up bromine and iodine by direct addition, forming crystalline, but very unstable, compounds. *Lutecobaltic salts* also unite with halogens (Gibbs).

*Lutecobaltic chloride*,  $12\text{NH}_3\cdot\text{Co}^2\text{Cl}^2$ .—Dana described the crystals of this salt as trimetric (i. 1055); but, according to recent measurements by C. Klein (*Ann. Ch. Pharm.* elxvi. 188) they are monoclinic, having the axes  $a : b : c = 1.7115941 : 1 : 1.1128766$ . Angle of inclined axes:  $b, c = 57^\circ 31' 9''$ . Principal angles:  $0\text{P} : +\text{P}\infty = 113^\circ 12'$ ;  $+ \text{P} : +\text{P}\infty = 151^\circ 45'$ ;  $\infty \text{P} : \infty \text{P} = 127^\circ 30'$ .

Observed forms (fig. 8):



more rarely:  $+\frac{1}{2}\text{P}, \infty \text{P}\infty$ , and as twin-face  $+\frac{1}{2}\text{P}\infty$ .

The crystals are sometimes tabular according to  $0\text{P}$ , sometimes prismatic according to  $\infty \text{P}$ , in the latter case with felspathic development. They seldom occur as simple individuals, but frequently as aggregates, some of

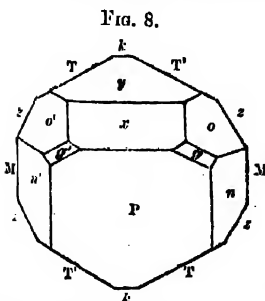


FIG. 8.

which may be referred to regular twin-combinations, in which either: (1) the twin-axis is the principal axis, and the combination face is  $\infty \text{P}\infty$ ; or (2) the twin-axis is the normal to  $+\frac{1}{2}\text{P}\infty$ ; twin and combination face  $+\frac{1}{2}\text{P}\infty$ . The combinations formed according to the first law are contact-twins, always implanted by the end which exhibits the re-entering dome-angles; those formed according to the second law are either contact or intersecting twins. Besides these regular combinations, others frequently occur which are formed with a certain regularity, but cannot, perhaps, be called twin-crystals in the ordinary sense of the word. Their structure may be understood by regarding them as formed according to

the following law:—Twin-axis normal to the base; combination- and twin-plane, the base; angle of rotation  $180^\circ$ .

The plane of the optic axes is perpendicular to the plane of symmetry, and the first positive median line is nearly at right angles to OP, while the second coincides with the orthodiagonal.

**Double salts of Luteocobaltic sulphate.**—When a solution of this salt is mixed with a very acid solution of cerous sulphate, a very beautiful light yellow crystalline precipitate is formed, having the composition  $12\text{NH}_4\text{Co}^2(\text{SO}_4)^2 + \text{Co}^2(\text{SO}_4)^2 + \text{H}_2\text{O}$ , and capable of bearing a heat of  $150^\circ$  without decomposition. When a neutral solution of cerous sulphate is mixed with luteocobaltic sulphate, a cerous double sulphate is formed, having the composition  $12\text{NH}_4\text{Co}^2(\text{SO}_4)^2 + 3\text{CeSO}_4 + \text{H}_2\text{O}$ . This salt forms small crystals undistinguishable under the microscope from those of the ceric double salt, and apparently isomorphous with them. Exactly similar cerous and ceric salts are formed with rosecobaltic sulphate. These, likewise, appear to be isomorphous, but they do not form measurable crystals (C. H. Wing, *Deut. Chem. Ges. Ber.* vi, 508).

**COBALT-YELLOW.** The yellow precipitate formed by the action of potassium nitrite on cobaltous salts was regarded by Stromeyer as a basic potassio-cobaltic nitrite,  $3\text{K}^2\text{O} \cdot \text{Co}^2\text{O}_3 \cdot 5\text{N}^2\text{O}^3$  or  $\text{K}^6(\text{Co}^2)^{10} \left\{ \begin{smallmatrix} (\text{NO}_2)^{10} \\ \text{O}'' \end{smallmatrix} \right\}$  (i. 1058). Erdmann, however, afterwards showed (*J. pr. Chem.* xvii. 385; *Jahresb.* 1866, 248) that the composition of the precipitate thus formed varies accordingly as the solution is acid or neutral: a neutral solution of cobaltous chloride yielding with excess of potassium nitrite a yellow crystalline precipitate of *potassio-cobaltous nitrite*  $3\text{CoK}^2(\text{NO}_2)^4 + \text{H}_2\text{O}$ , or  $3(\text{CoO} \cdot \text{N}^2\text{O}^3 + \text{K}^2\text{O} \cdot \text{N}^2\text{O}^3) + \text{H}_2\text{O}$ , its composition being the same whether the precipitation takes place in contact with the air or in an atmosphere of carbonic anhydride, whereas a solution mixed with excess of acetic acid yields salts of more complex and somewhat uncertain composition, containing, according to circumstances, either cobaltous or cobaltic oxide. These observations have been confirmed by Sadtler (*Sill. Am. J.* [2] xlix. 189), who finds that when a solution of cobaltous chloride strongly acidulated with acetic acid is mixed with a concentrated solution of potassium nitrite, a salt is formed which, after washing, first with potassium acetate and then with alcohol, has the composition of *tripotassio-cobaltic nitrite*  $\text{Co}^2\text{O}_3 \cdot 3\text{N}^2\text{O}^3 + 3(\text{K}^2\text{O} \cdot \text{N}^2\text{O}^3)$  or  $\text{Co}^2\text{K}^6(\text{NO}_2)^{12}$ . According to the concentration of the solution employed, it separates in combination with 4, 3, 2, 1 mol. water, or in the anhydrous state, the colour varying accordingly from light yellow to dark greenish-yellow. It is easy to see, therefore, that mixtures of these several hydrates will frequently separate out, and it is difficult to give an exact process for obtaining either of them in a definite state.

A solution of cobaltous chloride kept constantly acidulated with acetic acid yields, on addition of sodium nitrite, first a brown precipitate of *tetranodio-cobaltic nitrite*  $\text{Co}^2(\text{NO}_2)^6 + 4\text{NaNO}_2 + \text{H}_2\text{O}$ , and, on further addition of sodium nitrite, *triodio-cobaltic nitrite*  $\text{Co}^2(\text{NO}_2)^4 + 6\text{NaNO}_2 + \text{H}_2\text{O}$ . The solution of the latter salt mixed with luteocobaltic chloride yields a yellow crystalline salt insoluble in water, in which the sodium is replaced by luteo-cobalt, its formula being  $\text{Co}^2(\text{NO}_2)^4 + \text{Co}^2(\text{NH}_2)^{12}(\text{NO}_2)^6 + \text{H}_2\text{O}$ . In like manner are obtained the corresponding *rosecobaltic salt*  $\text{Co}^2(\text{NO}_2)^4 + \text{Co}^2(\text{NH}_2)^{10}(\text{NO}_2)^8$ , and a *xanthocobaltic salt* which, however, has not been analysed. The corresponding ammonium salts, viz., *tetrammonio-cobaltic nitrite*  $\text{Co}^2(\text{NO}_2)^6 + 4(\text{NH}_4)\text{NO}_2 + 2\text{H}_2\text{O}$ , and *hexammonio-cobaltic nitrite*  $\text{Co}^2(\text{NO}_2)^4 + 6(\text{NH}_4)\text{NO}_2 + 2\text{H}_2\text{O}$ , have also been obtained; but the conditions of their formation have not been ascertained further than that the hexammonio-compound is formed when strong solutions of ammonium nitrite and cobaltous chloride are employed. No substituted compounds have been obtained from these ammonio-salts.

A warm neutral solution of cobaltous chloride yields, on addition of a dilute solution of potassium nitrite, first a black or green crystalline precipitate of *potassio-dicobaltous nitrite*  $2\text{Co}(\text{NO}_2)^2 + 2\text{KNO}_2 + \text{H}_2\text{O}$ , afterwards a yellow, slightly crystalline or amorphous precipitate of *potassio-monocobaltous nitrite*  $\text{Co}(\text{NO}_2)^2 + 2\text{KNO}_2 + \text{H}_2\text{O}$ , the latter agreeing in composition with the salt which Erdmann obtained under similar circumstances, except in the amount of water (Sadtler).

**COBALTCYANIDES.** See CYANIDES.

**COCCOGNIN**,  $\text{C}^{20}\text{H}^{22}\text{O}^8$ . A colourless crystalline substance contained in the seeds of *Daphne Mezereum*. It is sparingly soluble in water, easily in alcohol and ether, sublimes when heated, emitting an odour like that of coumarin; it differs from daphnin by not yielding sugar when boiled with dilute sulphuric acid (Caselmann, *Zeitschr. f. Chem.* [2] vi. 681). See DAPHNE.

**COCHINEAL.** The following determinations of the composition of cochineal

and carmine, from various sources, have been made by C. Mène (*Compt. rend.* lxxiii 666):—

	Cochineal				Carmine			
	Guatemala	Canaries	So-called dead	Java	So-called Chère Vert	From Provence	From Spain	From Poland
Water and loss	4.700	6.060	4.135	8.033	7.214	6.435	6.855	6.217
Stearin . . .	8.155	10.131	3.090	4.255	3.108	2.925	2.935	3.120
Margarin . . .	8.451	8.293	3.007	3.108	1.435	1.409	1.517	2.006
Insol. matter	6.172	6.004	12.712	14.159	12.735	11.728	11.892	14.415
Nitrogenous matter	7.115	7.152	15.115	12.152	15.355	14.915	14.925	13.277
Substances soluble in water . . .	13.208	10.031	30.674	17.617	25.965	30.248	33.841	37.755
Colouring matter . . .	48.823	49.007	26.172	33.795	26.955	24.190	20.975	15.100
Ash . . .	3.376	3.322	5.065	6.210	6.233	8.150	7.060	8.080
	100.000	100.000	100.000	99.359	99.000	100.000	100.000	100.000

• **Colouring matter of Cochineal: Carmine or Carminic Acid.**—The salts of carminic acid are generally violet. Pure calcium carminate, however, is a black precipitate which appears greenish when in thin layers. It is formed by treating carminic acid or a decoction of cochineal with calcium bicarbonate. The precipitate produced is insoluble in water and in alcohol, but dissolves in concentrated acetic acid. In contact with an excess of lime-water the black carminate becomes deep violet, the solution also assuming the same colour. The lime employed in these experiments contained no traces of iron (Guignet, *Bull. Soc. Chim.* [2] xviii. 162).

*Testing.*—J. M. Merrick (*Pharm. J. Trans.* [3] i. 906; *Chem. Soc. J.* [2] ix. 501) compares the colouring power of different samples of cochineal by boiling equal weights of the samples with water for the same time (2 grams with 750 c.c. water for half an hour), and adding a weak solution of potassium permanganate to equal volumes of these decoctions till the original deep red colour changes to a very pale pink, almost yellow. The quantities of colouring matter in the samples thus treated are directly proportional to the quantity of permanganate required to produce this change of colour.

*Spectroscopic characters.*—An ammoniacal solution of carmine, examined by the spectroscope, exhibits two dark absorption-bands between the Fraunhofer lines D and E, like those of blood, one situated at 8°, the other at 9°–10° of a spectroscope having a scale of 20°, in which the sodium line falls at 7.7°. With such a spectroscope, therefore, it would be impossible to distinguish an ammoniacal solution of carmine from that of blood.

The aqueous solution of cochineal does not exhibit any dark bands, but on adding ammonia in quantity sufficient to give the solution a red colour inclining to violet, the two dark bands of the ammoniacal carmine solution make their appearance (Campani, *Gazzetta chimica italiana*, i. 471).

**Nitrococcus acid,  $C^6H^3(NO^3)_3O^2$ .**—This acid, which De La Rue obtained by the action of nitric acid on carminic acid (i. 804), may also be prepared by gradually adding finely powdered carmine to boiling nitric acid (sp. gr. 1.37) as long as the violent evolution of red vapours lasts. On cooling, the liquid solidifies to a mass of crystals of oxalic acid and nitrococcus acid, which are separated by recrystallisation from very dilute nitric acid. The nitrococcus acid is thus obtained in large silvery plates. On heating it with water in closed tubes to 180°, it splits up into carbon dioxide and trinitrocresol,  $C^6H^3(NO^3)_3OH$ , identical with that which Ducloux obtained from coal-tar cresol. This reaction shows that nitrococcus acid is one of the isomeric trinitrocresotic acids, and that the colouring matter of cochineal contains methylated benzene-residues (Liebermann & van Dorp, *Dent. Chem. Ges. Ber.* iv. 655).

**Rufococcin,  $C^6H^3O^2$ .**—On heating a solution of carmine in concentrated sulphuric acid, the yellowish-red colour of the solution changes at 120° into violet, carbon

dioxide and sulphur dioxide being evolved at the same time; and if, after the temperature has been kept for some time at 140°-150°, the liquid be poured into cold water, rufiococin is obtained as a brown precipitate, which may be purified by washing, drying, exhausting with boiling alcohol, and evaporating the solution.

It is very sparingly soluble in cold water; dissolves in alcohol with a fine yellow fluorescence. When heated it gives off red vapours which condense to yellowish-red needles. It yields a calcium-compound having the composition  $C^{14}H^{14}CaO^4$ .

By heating rufiococin with zinc-dust, a solid crystalline hydrocarbon,  $C^{16}H^{12}$ , is obtained, which sublimes in white plates, melting between 183° and 188°. It yields by oxidation a quinone resembling anthraquinone, but melting at 250° (anthraquinone melts at 275°).

Another body formed at the same time as rufiococin, by the action of sulphuric acid on carmine, appears to have the formula  $C^{22}H^{20}O^{12}$ ; and inasmuch as it yields, after heating with baryta-water, the same hydrocarbon as rufiococin, it appears to contain the same carbon-nucleus (Liebmann a. van Dorp, *ibid.* iv. 656; *Ann. Ch. Pharm.* clxiii. 97).

**Rufiocarmine**,  $C^{14}H^{12}O^4$ , another condensation-product of carmine-red, is formed by heating carmine with water. A dark resinous body is then deposited, from which rufiocarmine may be extracted by ether. It is a carmine-coloured powder, differing from carmine-red by its total insolubility in water, and from rufiococin by its extreme solubility in alcohol.

Rufiococin and rufiocarmine are intimately related to coccinin, the substance which Hlasiwetz a. Grabowski obtained by fusing carmine-red with potash (1st *Suppl.* 414). These chemists assigned to it the formula  $C^{24}H^{12}O^3$ , but their analytical numbers agree equally well with the formula  $C^{24}H^{16}O^4$ ; in fact, coccinin gives by analysis very nearly the same per-centage of carbon as rufiococin, and a larger proportion of hydrogen, as appears from the following comparison:—

	Rufiococin, according to Liebmann a. van Dorp					Coccinin, according to Hlasiwetz a. Grabowski			
C	61.10	63.58	63.78	63.93	61.47	61.8	61.3	61.5	65.0
H	4.51	4.05	3.66	3.76	3.67	4.8	4.3	4.3	4.7

It has not, however, been found possible to obtain coccinin from rufiococin or rufiocarmine by the action of sodium-amalgam or by fusion with alkali (Liebmann a. van Dorp).

**COCKCHAFER.** *Melolontha vulgaris*.—These insects contain, together with leucine and other substances, a colourless crystalline substance called melolonthine (*y. v.*).

**COCOA-NUTS.** The fatty matter extracted from these nuts is used almost exclusively for the manufacture of toilet soap. The cake left after the extraction of the fat is used in England as fodder for cattle, in Italy as manure.

The oil-cake of the cocoa-nut was examined some years ago by Grouven (*Wochenblatt der Annalen der Landwirtschaft*, 1866, p. 453), who found:—

In 100 parts of the air-dried oil-cake—

Proteids	Oil	Cellulose	Water
21.20	8.60	7.70	9.36;

and in 100 parts of the ash ( $CO^2$  deducted)—

K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>2</sup>	SiO <sup>2</sup>	Cl
40.67	2.30	4.71	2.95	3.54	26.08	3.78	3.38	13.42

As, however, the cocoa-nuts now sent to Europe are of selected quality, and more carefully freed from the other parts of the fruit than formerly, and as, moreover, many improvements have been made in the extraction of the fat, it has been thought worth while to make a fresh examination of the cocoa-nut and of the oil-cake, such as is obtained for the soap-works of Cav. Mazzuchetti, in Turin, and sent in large quantities to England as fodder for cattle:

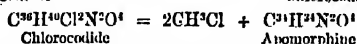
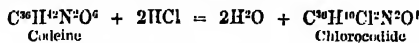
	Cocoa-nuts in the natural state	Oil-cake from Mazzuchetti's Soap-works
Water	5.80	11.60
Fat (extracted by CS <sup>2</sup> )	67.85	12.34
Cellulose	21.80	69.46
Mineral substances	1.55	6.11
	100.00	100.00

100 parts of the fresh oil-cake contain 2.75 p.c. nitrogen, and 100 parts of the cake contain 24.35 p.c. phosphoric anhydride (Nallino, *Gazzetta chimica italiana*, 11. 20).

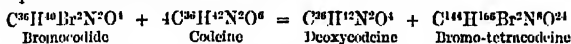


**CODANINE.** Hesse, in his latest communication on the opium-bases (*Ann. Ch. Pharm., Suppl.* viii. 261), assigns to this compound the formula  $C^{20}H^{23}NO$  instead of the former one  $C^{21}H^{23}NO$  (*1st Suppl.* 480). He finds that it melts at  $126^{\circ}$  when crystallised from benzene, and at  $121^{\circ}$  when crystallised from alcohol or ether; with ferric chloride it forms a dark green liquid, with separation of ferric oxide. It appears to form compounds with caustic alkalis.

**CODEINE.**  $C^{18}H^{21}NO^3$ , or  $C^{18}H^{19}NO^4$ . *Action of Hydrobromic acid* (Wright, *Proc. Roy. Soc.* xix. 371, 504).—It has been shown by Matthiessen and Wright (*1st Suppl.* 480) that when codeine is heated with a large excess of strong hydrochloric acid, the following reactions successively take place:—



When codeine is gently heated with hydrobromic acid, the first stage of the reaction appears to be similar to that of hydrochloric acid, yielding bromocodide,  $C^{31}H^{40}BrN^2O^4$ , analogous to chlorocodide; but this base appears to be further acted on with great ease, giving rise to two others, viz., deoxycodine,  $C^{35}H^{42}N^2O^4$ , soluble in ether, and bromo-tetracodine,  $C^{44}H^{66}Br^2N^2O^4$ , insoluble in ether. These reactions may be represented as follows:—



Moreover, the formation of bromocodido is preceded by that of a brominated base having the composition  $C^{16}H^{13}BrN^2O^4$ , the action in this respect also being analogous to that of hydrochloric acid.

Bromocodide is not easily obtained pure on account of the facility with which it is altered; but by digesting 1 part of codeine at 100° for an hour or two with 3 parts of acid solution (containing 48 p.c. HBr); precipitating with excess of sodium carbonate; filtering to remove excess of codeine, which remains dissolved; exhausting the precipitate with ether; and agitating the ethereal solution with hydrobromic acid, crude hydrobromide of bromocodide is produced; and by repeating the process and precipitating fractionally to remove colouring matters, the purified hydrobromide is obtained, yielding by analysis numbers agreeing nearly with the formula  $C^{10}H^{15}BrN^3O_2 \cdot 2HBr$ .

Crude hydrobromide of bromodecine, obtained by digesting ecdesine for five or six hours with from three to five times its weight of acid containing 48 p.c. HBr, deposits, on standing for some days, crystals not readily soluble in cold water; these recrystallised several times from boiling water, produce minute snow-white crystals which slightly darken in colour on drying over oil of vitriol, and on analysis give numbers agreeing with the formula of deoxyecdesine hydrobromide,  $C_{26}H_{42}N_2O_4 \cdot 2HBr$ .

**Bromotetracodecine** is conveniently obtained as hydrobromide by treating codeine with three times its weight of hydrobromic acid containing 48 p.c. HBr for two hours on the water-bath, precipitating the product (diluted with water) with excess of sodium carbonate, exhausting the well-drained precipitate with ether, dissolving the residue in the smallest possible quantity of weak hydrobromic acid, and fractionally precipitating by cautious addition of stronger acid. The second precipitate is dissolved in water, in which it is readily soluble, and a few drops of solution of sodium carbonate are added. The filtrate from this yields, with strong hydrobromic acid, nearly white flakes, which are wholly devoid of crystalline character under the microscope. These remain solid at 100°, if previously completely dried over oil of vitriol, but, if warmed while moist, are converted into a more or less coloured tar. Dried at 100°, they give numbers agreeing with the formula,  $C_{27}H_{45}BrN^{+}O^{12} \cdot 4HBr$ .

Sodium carbonate throws down from the hydrobromide a nearly white precipitate, which rapidly darkens, and finally becomes deep green or nearly black, owing to rapid absorption of oxygen; an analysis of the altered product gave the formula for bromotetradecine plus 9 atoms of oxygen; the salts, however, when dry, may be kept without alteration, and slowly darken by exposure to air only when moist.

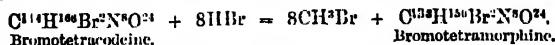
The qualitative reactions of bromotetradecine appear to be identical with those of bromo- and chloro-codide. The base itself, when freshly precipitated, is slowly soluble in water, being thrown down again by the addition of strong brine; in ether and benzene it is almost insoluble, and in alcohol but sparingly soluble.

When crude bromotetracadeine is dissolved in weak hydrochloric acid, and precipitated twice or thrice by excess of stronger acid, nearly white flakes are ultimately obtained, which, when dried over oil of vitriol and finally at 100°, have the composition of the hydrochloride of chlorotetracadeine,  $C_{14}H_{18}ClNO \cdot 8HCl$ .

Chlorotetracodeine, in all its physical and chemical properties, closely resembles  
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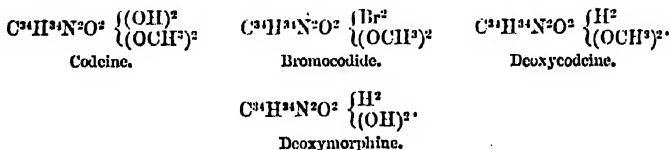
bromotetracodeine<sup>\*</sup>; the qualitative reactions of the two bases are identical, they have an intensely bitter taste, and apparently but slight physiological action, at any rate in small doses.

When hydrobromide of bromotetracodeine is heated with hydrobromic acid, the homologous base bromotetramorphine is produced, with elimination of hydrogen bromide:—



By the action of hydrochloric acid in the cold on bromotetramorphine, the corresponding chlorinated base, chlorotetramorphine, is formed; and by interrupting the action of hydrobromic acid on codeine at a certain point, a base intermediate between bromotetramorphine and bromotetracodeine appears to be formed; and this, by the action of hydrochloric acid, is converted into the corresponding chlorinated base chloro-dicodeno-dimorphine,  $\text{C}^{10}\text{H}^{106}\text{Cl}^2\text{N}^2\text{O}^2$ .

By the action of hydrobromic acid on bromocodide, methyl bromide is formed, and simultaneously bromotetramorphine, and apparently a base, deoxymorphine,  $\text{C}^{10}\text{H}^{106}\text{N}^2\text{O}^2$ , homologous with deoxycodeine; this latter, like its homologue, much resembles apomorphine in chemical characters, but produces no vomiting; it is doubtful whether deoxymorphine has been obtained perfectly free from deoxycodeine. From these results, taken in conjunction with former ones, the following formulæ are ascribed to the corresponding bases:—

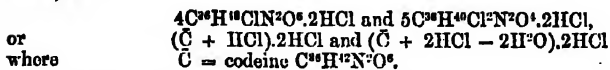


Deoxymorphine does not seem to be produced by the action of hydrobromic acid on deoxycodeine, the only product being a black substance unfit for analysis, along with a little methyl bromide.

Dr. Michael Foster has examined the physiological action of the foregoing derivatives, and finds that the chloro- and bromotetracodeine and tetramorphine salts produce in adult cats a condition of great excitement, almost amounting to delirium in younger animals; a want of co-ordination of muscular movements follows, terminating in sleepiness, stupor, and death. Paralysis of the inhibitory fibres of the pneumogastric appears to be produced in cats and dogs; with rabbits all these salts appear to be almost inert.

Deoxycodeine and deoxymorphine salts are absolutely destitute of emetic properties; in adult cats they produce convulsions of an epileptic character, followed by the symptoms observed in the case of the tetra-bases. No marked difference could be detected between the hydrobromides and hydrochlorides of either base; whereas with the tetra-bases, the morphine-compounds appeared to be rather more potent than their higher homologues.

*Action of Hydrochloric Acid.*—By acting for 2½ hours on codeine with 6 to 8 parts of strong hydrochloric acid a viscid uncrystallisable product is obtained, which is inferred from its analysis to be a mixture of the hydro-chlorides of two chlorinated bases, viz.:

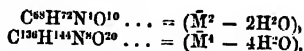


From these mixed hydrochlorides sodium carbonate throws down a mixture of the bases  $\bar{\text{C}} + \text{HCl}$  and  $\bar{\text{C}} + 2\text{HCl} - 2\text{H}^2\text{O}$ , both of which are soluble in ether, and form non-crystalline salts; the second is identical with chlorocodide derived from codeine by substitution of  $\text{Cl}^2$  for  $2\text{H}^2\text{O}$ .

It thus appears that the formation of chlorocodide is preceded by that of a base containing only 1 atom of chlorine to 36 atoms of carbon, and consequently chlorocodide must be represented by a formula containing  $\text{C}^{36}$  at least; but as ordinary codeine is formed from chlorocodide by the action of water (1st Suppl. 480), chlorocodide must be a derivative of ordinary codeine, and not of any of its higher polymers, and consequently the molecule of codeine must also contain 36 atoms carbon.

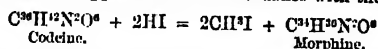
By the long-continued action of hydrochloric acid on the mixture of bases produced

as above, different results are obtained according to the circumstances of the experiment. Matthiessen & Wright showed (1st Suppl. 839), that by acting on codeine in sealed tubes at 140°-150° with strong hydrochloric acid, methyl chloride is formed, and apomorphine results, *identical with that obtained from morphine*. When, however, the action is allowed to take place at 100°, different bodies result; methyl chloride is eliminated, but the elements of water are not removed to such an extent as to produce apomorphine, two isomeric bases being then formed, intermediate in composition between morphine and apomorphine. One of these bases yields crystalline salts, and is readily soluble in ether; the other is insoluble in that liquid, and gives amorphous salts, and evidently belongs to the 'tetra' series. The two bodies are, therefore, considered to have respectively the formulæ:



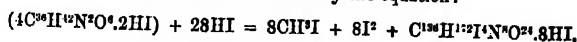
and are respectively termed *diapo-dimorphine* and *tetrapo-tetramorphine*. In physiological effects, diapo-dimorphine does not resemble tetrapo-dimorphine (apomorphine), the experiments of Dr. J. G. Blackley indicating that doses of 0.1 gram given subcutaneously to cats do not produce vomiting but only profuse salivation. The removal of the elements of water from (hypothetical) dimorphine and from tetramorphine gives rise to a different kind of alteration in the physiological effect (on cats) of the resulting product, the emetic action being *less* in the first case the more of the elements of water are removed, and *more* so in the second case.

*Action of Hydriodic Acid on Codeine in presence of Phosphorus* (Wright, *Proc. Roy. Soc.* xx, 8). The first action appears to be in accordance with the equation:

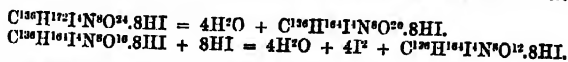


the quantity of methyl iodide evolved being close upon that required by theory; this evolution of methyl iodide does not take place however in the absence of phosphorus, much iodine being set free in that case.

According to the action of hydriodic acid (3 to 5 parts of 50 per cent. acid) and phosphorus ( $\frac{1}{15}$  part) upon codeine (1 part) takes place at 100° or at higher temperatures, different products are obtained, all of which may be considered as derived from morphine hydriodide by quadruplication of the molecule, addition of hydrogen and hydriodic acid to the product, and further alteration of the resulting compound by successive subtraction of the elements of water and of oxygen. Thus, if the reaction takes place at 100°, the product may be viewed as formed by the equation:

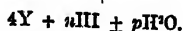
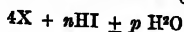


If the mixture be gently boiled so that the boiling point rises to 110°-115° by the time that methyl iodide ceases to be evolved, the product obtained contains 4H<sup>2</sup>O less than this formula; whilst, if the boiling be performed rapidly, so that the boiling point rises to 130°-135°, the end-product contains O<sup>8</sup> less than this latter body: thus—

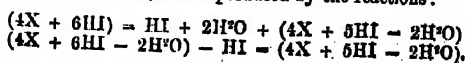


These three substances much resemble each other; they form colourless tarry masses, which rapidly become yellow by exposure to air; when quite dry they do not soften at 100°; water dissolves them with decomposition; from the solution bases derived from the original compounds by subtraction of the elements of HI may be obtained. Their qualitative reactions are identical with those of their derivatives, but utterly different from those of the codeine derivatives previously examined.

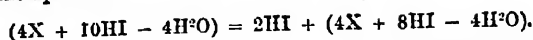
Denoting a hypothetical base, C<sup>34</sup>H<sup>40</sup>N<sup>2</sup>O<sup>4</sup>, by the symbol X, and another, C<sup>34</sup>H<sup>42</sup>N<sup>2</sup>O<sup>6</sup>, by the symbol Y, these three bodies and their derivatives may be all included in one or other of the two general formulæ:



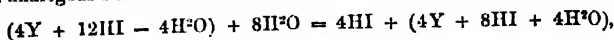
By dissolving the product obtained at 100° (4X + 12HI) in boiling water and boiling for some time, flakes of a peculiar microscopical structure are obtained on cooling the liquid; the same product is also formed from the substance obtained at 110°-115° by similar treatment, and is produced by the reactions:



On similarly treating the substance thus obtained, a further reaction takes place, indicated by the equation :



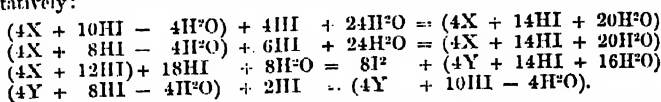
If the original product formed at 130°-135° be treated in like manner, it finally yields an analogous substance formed by the reaction :



the elements of 8 molecules of water being thus taken up.

On treating the original codeine-products with alkalis, the same reactions appear to ensue : yielding the free bases  $(4X + 2HI - 4H^2O)$ ,  $(4X + 4HI)$  and  $(4X - 4H^2O)$ . Of these the one containing no iodine is least soluble in ether, and the one containing most iodine is the most soluble ; they readily absorb oxygen from the air.

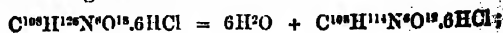
On again subjecting these derivatives formed by water or alkalis to the action of hydriodic acid, bodies are produced, not identical with those first obtained from codeine, but still belonging to the same family, and denoted by the same general formulæ. The reactions represented by the following equations have been verified quantitatively :



*Polymerisation of Codeine by the action of Phosphoric Acid.*—When codeine is polymerised by the action of hydrobromic or hydriodic acid, as in the reactions previously described, part of the hydrogen in the polymeride is always replaced by bromine or iodine, forming such products as bromotetracodeine, di-iodotetracodeine, &c. By the action of phosphoric acid, however, polymerides are formed without the occurrence of these substitutions. When 1 part of codeine, 3 of glacial phosphoric acid, and 5 of water, are very gently boiled in an open vessel until the temperature rises to nearly 200°, a considerable quantity of the codeine becomes polymerised, forming simultaneously *dicodeine*  $C^{12}H^{18}N^2O^{12}$ , and *tetracodeine*  $C^{14}H^{22}N^2O^{14}$ , which are sharply distinguished from codeine and from each other by their physical properties and chemical reactions. The first of these bases forms a crystalline hydrochloride, whose water of crystallisation is lost at 100°, the base itself being amorphous and immediately precipitated from its salts by sodium carbonate; whereas codeine is crystalline, and not immediately precipitated by sodium carbonate, and its hydrochloride, as shown by Matthiessen and Wright (*Proc. Roy. Soc.* xviii. 87), loses none of its water of crystallisation on drying over the water-bath at a temperature probably a little below 100°. Tetracodeine is amorphous, forms amorphous salts, and differs from codeine and dicodeine by being insoluble in ether.

These polymerides, obtained by the action of phosphoric acid, appear to be identical with the products formed by treating codeine with dilute sulphuric acid, viz., dicodeine with the amorphous isomeride of codeine which Armstrong obtained by heating codeine with dilute sulphuric acid for a short time only (*Chem. Soc. J.* [2] ix. 56), and tetracodeine with the amorphous codeine which Andersen obtained by the prolonged action of the same reagent (*Ed. Phil. Trans.* xx. [1] 57). On repeating the processes of these chemists, Wright obtained products apparently identical with those of the action of phosphoric acid, with this difference only, that Armstrong's process appears to give rise to a small quantity of another polymeride (in addition to dicodeine), which is non-crystalline and soluble in ether. Its hydrochloride utterly refuses to crystallise, and its reactions are different from those of either of the other polymerides. The dicodeine is separable from this by repeated crystallisation of its hydrochloride until the salt ceases to give a blood-red coloration on addition of nitric acid, the tint produced by pure dicodeine being a yellow orange, not intense. From the circumstance that in many instances this polymeride exhibits similarity to dicodeine, but in others to tetracodeine, Wright regards it as probably intermediate, i.e. as *tricodeine*,  $C^{10}H^{12}N^2O^{11}$ .

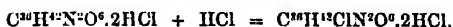
Hydrochloric acid acts on these polymerides very differently. On tetracodeine it has no action whatever after six hours' ebullition ; with tricodeine at 100° for 1½ hours it produces the following reaction :—



and with dicodeine the following :—



With codeino, as already observed, the first action appears to be to form an addition-product, thus:—



from which water is subsequently eliminated.

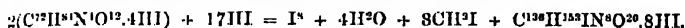
The composition of these chlorinated derivatives affords further proof that the lowest admissible formula of codeine is  $C^{20}H^{19}N^2O^6$ , and that of diocodeine  $C^{22}H^{19}N^2O^{12}$ . The reactions of tetracodeine, as shown below, lead to  $C^{24}H^{19}N^2O^{24}$  as its lowest formula. The product  $C^{20}H^{19}N^2O^{12}$  from tricodeine much resembles in its properties the apocodeine of Matthiessen and Burnside (*1st Suppl.* 481), produced by the action of zinc chloride on codeine; probably, therefore, this action gives rise to a mixture of 'apo' derivatives of the general formula  $(C^{18}H^{19}NO^2)_n.HCl$ , in which the derivative  $n = 6$  predominates.

Hydriodic acid, in conjunction with phosphorus, acts differently on diocodeine and tetracodeine. Tetracodeine hydriodide boiled with hydriodic acid till the boiling point rises to  $130^\circ$  is decomposed as shown by the equation:



the product being the hydriodide of a tetra-base insoluble (or nearly so) in ether.

Diocodeine becomes polymerised to a tetra-base nearly insoluble in ether, but in addition to methyl-elimination, hydrogen-addition takes place:—



the formula of the product proving that the minimum formula of tetracodeine must contain  $C^{18}$  and not  $C^{22}$  only. The hydrogen-addition, however, does not go so far as it does when ordinary codeine is employed; thus:—

Codeine at $100^\circ$	produces . . .	$8(C^{17}H^{19}NO^3 + H^2)$	+ 12HI
" " $110^\circ$ – $115^\circ$	" . . .	$8(C^{17}H^{19}NO^3 + H^2)$	+ 12HI – $4H_2O$
" " up to $130^\circ$	" . . .	$8(C^{17}H^{19}NO^3 + H^2 - O)$	+ 12HI – $4H_2O$
Diocodeine " $120^\circ$	" . . .	$8(C^{17}H^{19}NO^3 + H)$	+ 9HI – $4H_2O$
Tetracodeine " $130^\circ$	" . . .	$8(C^{17}H^{19}NO^3)$	+ 10HI – $2H_2O$ .

Hence diocodeine is in this respect strictly intermediate between codeine and tetracodeine.

The following table exhibits the principal differences between codeine and its polymers, above described:—

Reagent, &c.	Codeine	Diocodeine	Tricodeine	Tetracodeine
Alcohol.	Soluble.	Soluble.	Soluble.	Soluble.
Ether.	Soluble.	Soluble.	Soluble.	Insoluble.
Character of base.	Crystalline; stable in the air.	Amorphous; stable in the air.	Amorphous; very slowly oxidises while moist.	Amorphous; very slowly oxidises while moist.
Character of hydrochloride.	Crystallises with $2H_2O$ for $C^{18}$ ; not lost at $100^\circ$ .	Crystallises with $3H_2O$ for $C^{18}$ ; lost at $100^\circ$ , and partially at lower temperatures.	Non-crystalline; extremely deliquescent.	Non-crystalline; deliquescent.
Ferric chloride.	Nil.	Nil, when pure.	No colour at first; reddish-purple on standing.	Reddish-purple colour immediately.
Nitric acid.	Light orange.	Light orange.	Blood-red.	Blood-red.
Potassium dichromate and sulphuric acid.	Nil.	Nil.	Evanescent red.	Evanescent red.
Sodium carbonate and solution of hydrochloride.	No immediate precipitate; crystals on standing.	Instantaneous amorphous precipitate, but little soluble in excess.	Same as diocodeine.	Same as diocodeine.

Reagent, &c.	Codeine	Dicodeine	Tricocodeine	Tetracocodeine
Caustic potash and solution of hydrochloride.	Oily precipitate if concentrated, becoming crystalline on standing; not markedly soluble in excess.	Oily precipitate if concentrated, not becoming crystalline, more dilute solutions give a white amorphous precipitate, soluble in large excess.	Same as dicodeine.	Same as dicodeine.
Action of hydrochloric acid not pushed to extreme.	Product contains Cl for C <sup>36</sup> ; after further action it contains Cl <sup>2</sup> for C <sup>36</sup> .	Product contains Cl for C <sup>32</sup> .	H <sup>2</sup> O removed for C <sup>18</sup> ; product contains no basic Cl.	Nil.
Action of hydrochloric acid in conjunction with phosphorus.	Polymerises to tetra series, forming bases derived from (C <sup>17</sup> H <sup>21</sup> NO <sup>3</sup> ) <sub>4</sub> , or (C <sup>17</sup> H <sup>21</sup> NO <sup>2</sup> ) <sub>4</sub> , H <sup>1</sup> being added on for C <sup>17</sup> in product, and ClH <sup>2</sup> evolved for C <sup>18</sup> in original.	Polymerises to tetra series, forming bases derived from (C <sup>17</sup> H <sup>21</sup> NO <sup>3</sup> ) <sub>4</sub> , H <sup>1</sup> being added on for C <sup>17</sup> in product, and ClH <sup>2</sup> evolved for C <sup>18</sup> in original.	---	H <sup>2</sup> O removed, and H <sup>1</sup> added on (or I substituted for OH), no H <sup>1</sup> added on; ClH <sup>2</sup> removed for C <sup>18</sup> in original.
Action of sulphuric acid not pushed to extreme.	Polymerises, forming successively di-, tri-, and tetracodeine.	Polymerises, forming tetracodeine.	—	Nil; further action probably dehydrates and oxidises.
Formula inferred from above properties and reactions.	C <sup>36</sup> H <sup>42</sup> N <sup>2</sup> O <sup>4</sup> .	C <sup>32</sup> H <sup>38</sup> N <sup>2</sup> O <sup>12</sup> .	C <sup>108</sup> H <sup>120</sup> N <sup>6</sup> O <sup>18</sup> .	C <sup>144</sup> H <sup>168</sup> N <sup>6</sup> O <sup>24</sup> .
Physiological action of 0.1 gram of anhydrous hydrochloride, subcutaneously injected into adult cats.	Extreme hypersensitiveness and cerebral congestion; dilation of pupils; no diarrhoea; no vomiting in any instance.	No hypersensitiveness or cerebral congestion; dilation of pupils; vomiting in every instance.  With a dog, profuse diarrhoea, without vomiting.	Hypersensitiveness scarcely marked; vomiting in some instances, in others salivation and defecation.	No hypersensitiveness; vomiting, salivation, or diarrhoea in every case; great depression.  With a dog, profuse salivation and depression.

The following table, in which  $\bar{C}$  stands for codeine, and  $\bar{M}$  for morphine, exhibits the composition of the derivatives and polymerides of codeine above described, together with their origin and their relations to codeine:—

#### DERIVATIVES CONTAINING $\pi C^{36}$ (CODEINE SERIES).

Name.	Formula.	Origin.	Relation to Codeine.
Codeine . .	C <sup>36</sup> H <sup>42</sup> N <sup>2</sup> O <sup>4</sup> .	—	$\bar{C}$
—	C <sup>36</sup> H <sup>44</sup> ClN <sup>2</sup> O <sup>4</sup> .	Codeine and HCl.	$\bar{C} + \text{HCl}$
Chlorocodide .	C <sup>36</sup> H <sup>44</sup> Cl <sup>2</sup> N <sup>2</sup> O <sup>4</sup> .	Do. do.	$\bar{C} + 2\text{HCl} - 2\text{H}^2\text{O}$
—	C <sup>36</sup> H <sup>44</sup> BrN <sup>2</sup> O <sup>4</sup> .	Do. and HBr.	$\bar{C} + \text{HBr}$
Bromocodide .	C <sup>36</sup> H <sup>44</sup> Br <sup>2</sup> N <sup>2</sup> O <sup>4</sup> .	Do. do.	$\bar{C} + 2\text{HBr} - 2\text{H}^2\text{O}$

## DERIVATIVES—continued.

*Di Series.*

Name.	Formula.	Origin.	Relation to Codeine.
Dicocodeine .	$C^{72}H^{84}N^4O^{12}$ .	{ Codeine and $H^2PO^4$ .	$\bar{C}^2$ .
—	$C^{72}H^{82}ClN^4O^{11}$ .	{ Do. and $H^2SO^4$ .	
		Dicocodeine and HCl.	$\bar{C}^2 + HCl - H^2O$ .

*Tri Series.*

Tricocodeine .	$C^{108}H^{120}N^6O^{18}$ .	Codeine and $H^2SO^4$ .	$\bar{C}^3$ .
—	$C^{108}H^{114}N^6O^{12}$ .	Tricocodeine and HCl.	$\bar{C}^3 - 6H^2O$ .

*Tetra Series.*

Tetracocodeine .	$C^{144}H^{168}N^8O^{24}$ .	{ Codeine and $H^2PO^4$ .	
		{ Do. and $H^2SO^4$ .	$\bar{C}^4$ .
		{ Dicocodeine and $H^2SO^4$ .	

## DERIVATIVES FROM BASES MORE HYDROGENISED THAN CODEINE.

 $(\bar{C} + H^4)^2$  Series.

Deoxycocodeine.	$C^{72}H^{81}N^4O^8$ .	Codeine and HBr.	$(\bar{C} + H^4)^2 - 4H^2O$ .
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## DERIVATIVES FROM BASES LESS HYDROGENISED THAN CODEINE.

 $(\bar{C} - H)^4$  Series.

Bromotetra- codeine .	$C^{144}H^{166}Br^2N^8O^{24}$ .	Codeine and HBr.	$(\bar{C} - H)^4 + 2HBr$ .
Chlorotetra- codeine .	$C^{144}H^{166}Cl^2N^8O^{24}$ .	{ Bromotetracodeine and HCl.	$(\bar{C} - H)^4 + 2HCl$ .

DERIVATIVES CONTAINING  $2C^{34}$  (MORPHINE SERIES OF BASES DERIVED FROM CODRINE AS STARTING-POINT).*Di Series.*

Apomor- phine .	$C^{68}H^{68}N^4O^8$ .	{ Codeine and HCl at $150^\circ$ .	$\bar{M}^2 - 4H^2O$ .
(Tetrapodi- morphine).		{ Chlorocodide and do.	
Biapodimor- phine .	$C^{68}H^{72}N^4O^{10}$ .	{ Codeine and HCl at $100^\circ$ .	$\bar{M}^2 - H^2O$ .

*Tetra Series.*

Tetrapo- tetramor- phine .	$C^{136}H^{144}N^8O^{26}$ .	{ Codeine and HCl at $100^\circ$ .	$\bar{M}^4 - 4H^2O$ .
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## DERIVATIVES FROM BASES MORE HYDROGENISED THAN MORPHINE.

 $(\bar{M} + H^4)^2$  Series.

Deoxymor- phine .	$C^{96}H^{76}N^4O^6$ .	{ Codeine and HBr. Bromocodide and HBr.	$(\bar{M} + H^4)^2 - 4H^2O$ .
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 $(\bar{M} + H^2)^4$  Series.

—	$C^{126}H^{122}N^6O^{20}$ .	Dicocodeine, HI, and P.	$(\bar{M} + H^2)^4 + HI - 4H^2O$ .
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 $(\bar{M} + H^4)^4$  Series.

—	$C^{126}H^{122}N^4O^{24}$ .	{ Codeine, HI, and P at $100^\circ$ .	$(\bar{M} + H^4)^4 + 4HI$ .
—	$C^{126}H^{124}N^4O^{26}$ .	{ Do. do. at $115^\circ$ .	$(\bar{M} + H^4)^4 + 4HI - 4H^2O$ .

## DERIVATIVES—continued.

 $(\bar{M} + H)^1$  Series—continued.

Name.	Formula.	Origin.	Relation to Codeine.
Deoxymorphine.	$C^{136}H^{162}I^{22}N^8O^{20}$ .	{ Proceeding, treated } { with water. }	$(\bar{M} + H)^1 + 2HI - 4H^2O$ .
—	$C^{136}H^{161}I^{22}N^8O^{20}$ .	Do.	$(\bar{M} + H)^1 + HI - 4H^2O$ .
—	$C^{136}H^{160}I^{22}N^8O^{20}$ .	Do. do.	$(\bar{M} + H)^1 - 4H^2O$ .

 $(\bar{M} + H)^1$  Series.

—	$C^{136}H^{161}I^{22}N^8O^{12}$ .	{ Codeine, III, and P } { at 135°.	$(\bar{M} + H)^1 + 4HI - 12H^2O$ .
—	$C^{136}H^{159}N^8O^{12}$ .	Proceeding and water.	$(\bar{M} + H)^1 - 4H^2O$ .
—	$C^{136}H^{158}I^{22}N^8O^{21}$ .	Do. and HI.	$(\bar{M} + H)^1 + 2HI - 4H^2O$ .

## DERIVATIVES FROM BASES LESS HYDROGENISED THAN MORPHINE.

 $(\bar{M} - H)^1$  Series.

Bromotetra- morphine. }	$C^{136}H^{150}Br^{22}N^8O^{24}$ .	{ Codeine and HBr. } { Bromocodide and } { HBr. }	$(\bar{M} - H)^1 + 2HBr$ .
Chlorotetra- morphine. }	$C^{136}H^{150}Cl^{22}N^8O^{24}$ .	{ Bromotetramor- phine and HCl. }	$(\bar{M} - H)^1 + 2HCl$ .

**COERULIGNONE**,  $C^{136}H^{160}O^6$  or  $C^{22}H^{29}O^{12}$  (Liebmann, *Deut. Chem. Ges. Ber.* v. 746; vi. 381). A blue substance obtained as a bye-product in the manufacture of wood-vinegar.

The crude calcium acetate obtained by neutralising with lime the acid liquor produced by the distillation of wood, is in practice decomposed by distillation with the requisite quantity of hydrochloric acid, the crude acetic acid thus obtained being purified by the addition of potassium bichromate. Under these circumstances the crude acetic acid deposits blue films, which sink to the bottom as a violet sediment. The substance thus deposited is purified first by elutriation, and afterwards by dissolution in cold phenol, from which it is precipitated by alcohol or ether. The precipitate thus obtained consists of pure coerulignone.

Coerulignone crystallises in small dark steel-blue needles. It is insoluble in all the ordinary solvents, and neither distils nor sublimes without change. It dissolves with blue colour in concentrated sulphuric acid, but has not been separated from the solution in its original state. It neither dyes with nor without a mordant. With acetic anhydride it yields a crystalline product, and when treated with nitric acid it is oxidised to oxalic acid. Heated with potash-solution it gives a green liquid, which quickly becomes yellow. If the solution be concentrated till the potash begins to fuse, a point is reached at which the mass dissolves in water with an intense but fugitive violet colour. The action of hydriodic acid and phosphorus at 160° gives rise to the same colouring substance as that which is produced by the action of potash. This product, when dissolved in ether, yields an almost colourless solution, and is deposited in the amorphous state when the solution is evaporated in a vacuum: to an alkaline solution it communicates an intense but evanescent violet coloration.

The formation of coerulignone was observed on the addition of potassium bichromate to a variety of samples of crude acetic acid, but it has not yet been ascertained whether the acetic acid obtained from all kinds of wood yields this substance; it has, however, been obtained from the acid resulting from the distillation of both birch and beech wood.

**Hydrocoerulignone**,  $C^{136}H^{160}O^6$ , is obtained by the action of tin and hydrochloric acid, potassium hydrate, ammonium sulphide, sulphurous acid, or sodium-amalgam on coerulignone. It crystallises well, is soluble in alcohol and acetic acid, and less so in water. It melts at 190°, and may be distilled almost without change if carefully heated. The distillate solidifies to long colourless crystals. It is also volatile to a certain extent with the vapour of acetic acid. It is converted into coerulignone by oxidising agents, and forms compounds with acetic anhydride and benzoyl chloride. Concentrated sulphuric acid dissolves it, producing an orange colour, which is changed by heating into fuchsine red.

Hydrocoerulignone contains two replaceable hydrogen-atoms. The addition of potassium ethylate to its alcoholic solution producing an egg-yellow precipitate



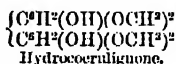
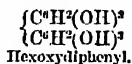
$C^{12}H^{10}K^{2}O^6$ , and sodium ethylate forms a similar precipitate  $C^{12}H^{10}Na^{2}O^6$ . *Benzoyl-hydrocoerulignone*  $C^{16}H^{14}(C^7H^5O)^2O^6$ , obtained either by the action of benzoic chloride on hydrocoerulignone, or by heating that compound with benzoic anhydride to  $150^{\circ}$ – $160^{\circ}$  in an open flask by means of an oil-bath, crystallises in prisms resembling sublimed benzoic acid, sparingly soluble in alcohol, melting at  $244^{\circ}$ . The *acetyl-derivative*  $C^{16}H^{14}(C^2H^3O)^2O^6$  forms white crystals slightly soluble in alcohol, melting at  $216^{\circ}$ .

When hydrocoerulignone is heated with hydrochloric acid in sealed tubes, methyl chloride is formed, together with hexoxydiphenyl,  $C^{12}H^{10}O^6$ .

Hexoxydiphenyl forms magnificent, glistening, colourless crystals, grouped in rosettes. It is soluble in most solvents. Its solutions in alkalis have a splendid purple colour, which however appears to be the result of oxidation. With metallic acetates it yields violet to blue unstable precipitates, that produced by cadmium acetate being the most finely coloured.

A crystalline *hexacetyl-derivative*  $C^{12}H^{10}(C^2H^3O)^6O^6$ , and the corresponding *propionyl-derivative* are obtained by treating the compound with the chlorides of acetyl and propionyl. The *benzoyl* and *isobutyryl* derivatives have not been obtained pure. Hexoxydiphenyl is decomposed when passed over heated zinc-dust, yielding diphenyl.

Liebermann regards hexoxydiphenyl as a dipyrrogallol, and hydrocoerulignone as its tetramethyl-derivative:



Whether coerulignone is the quinone  $C^{16}H^{10}O^6$ , or the quinhydrone  $C^{32}H^{20}O^{12}$ , of hydrocoerulignone is not yet determined.

Coerulignone or hydrocoerulignone treated with strong sulphuric acid, yields two compounds,  $C^{12}H^{10}O^6$  and  $C^{12}H^{12}O^6$ , intermediate between coerulignone and hexoxydiphenyl. The first forms yellow needles; the second, which results from prolonged action of the acid, is an amorphous orange-coloured powder. These compounds may be regarded as coerulignone in which one and two atoms of methyl are replaced by hydrogen.

To ascertain from which constituent of wood coerulignone is produced, pure cellulose (Swedish filter-paper or unbleached calico), oak-bark and beech-wood were severally subjected to dry distillation. Pure cellulose yielded no coerulignone; 2 lbs. of oak-bark yielded only doubtful traces; but from 2 lbs. of beech-wood no less than half a gram of pure coerulignone was isolated, thus showing that it is derived from some peculiar constituent of beech-wood.

**COFFEE.** The ash of the undermentioned parts of the coffee-tree grown in Brazil has been analysed by H. Ludwig (*Arch. Pharm.* [3] i. 482), with the following results:—

	I.	II.	III.	IV.	V.	VI.	VII.
K <sup>2</sup> O . . . .	16.24	3.99	14.95	15.56	15.87	14.13	44.03
Na <sup>2</sup> O . . . .	2.18	6.66	1.13	trace	5.10	5.84	5.85
CaO . . . .	27.04	38.04	20.82	16.83	21.02	8.64	4.89
MgO . . . .	4.15	5.30	7.96	5.63	4.62	8.14	8.01
Fe <sup>2</sup> O <sup>3</sup> . . . .	3.39	5.03	3.58	11.38	7.12	16.54	1.96
Mn <sup>2</sup> O <sup>3</sup> . . . .	0.44	trace	0.40	trace	—	trace	trace
Al <sup>2</sup> O <sup>3</sup> . . . .	7.85	1.59	9.11	trace	4.19	2.78	trace
SiO <sup>2</sup> . . . .	6.16	1.23	0.60	15.16	9.25	1.65	0.37
CO <sup>2</sup> . . . .	27.55	25.16	21.03	20.13	13.28	8.34	21.24
P <sup>2</sup> O <sup>5</sup> . . . .	2.28	11.30	6.23	9.99	16.70	18.65	10.54
SO <sup>3</sup> . . . .	2.26	1.38	3.99	3.94	1.95	15.28	1.64
Cl . . . .	1.05	0.25	1.56	1.34	trace	trace	0.98
I . . . .	—	—	—	0.88	—	—	—
	100.59	100.02	100.30	100.84	100.00	99.99	99.51

I. Root of a young tree in bearing. II. Root of an old tree. III. Leaves. IV. Pulp of the pericarp. V. Parchment-like coating of coffee-beans. VI. Coffee-beans grown on gneiss soil. VII. Coffee-beans grown on limestone soil.

The amount of phosphoric acid in young trees increases from the root to the fruit and its separate parts. The increased proportion of this acid in the roots of old trees is remarkable.

From analyses of the ash of coffee-beans of various growths made by Graham, Stenhouse, and Campbell (i. 1071) these chemists inferred that sodium-compounds and silica are entirely wanting in that part of the tree. The inference is not borne out by the present analyses, which show the presence of considerable quantities of sodium. The silica found by Ludwig in the ash of the beans may, he thinks, be derived from small quantities of adhering earth; but that silica is an essential constituent of other parts of the tree is clearly shown by the fact that it increases in amount from the root to the leaves and pulp, decreases in the parchment-like coating of the beans, and suddenly disappears in the beans themselves.

The influence of the soil upon the ash-constituents is shown in a marked manner in the amount of potash, iron, &c., in columns VI. and VII.

**COLLIDINE**,  $C^8H^{11}N$ , is formed by the action of chlorethylidene on ammonia. When chlorethylidene, prepared either from aldehyde and pentachloride of phosphorus or from ethyl chloride and chlorine, is heated to  $160^\circ$  in a sealed tube with alcoholic ammonia, the tube becomes filled in the course of twelve hours with crystals of sal-ammoniac; and the alcohol holds in solution an oily base which, if aqueous instead of alcoholic ammonia be used, separates at once as a layer above the sal-ammoniac. When dried over potash and rectified, it boils at  $180$ – $182^\circ$ , and in odour and in the characters of its beautifully crystallised platinum salt, it exhibits entirely the characters of collidine. This base and sal-ammoniac appear to be only products of the reaction (Krämer, *Zeitschr. f. Chem.* [2] vi. 568).

Collidine is also found among the products of the decomposition of aldehyde-ammonia by acids (Krämer & Pinner, *ibid.* 470).

**COLLODION**. A very tenacious collodion may be prepared by dissolving collodion-pyroxilin in a mixture of ether and absolute alcohol, and adding a small quantity of copaiba balsam (Böttger, *Chem. Centr.* 1872, 745). On the preparation of collodion for photography, see also *Chem. Soc. J.* [2] x. 272, 533.—On the preparation of collodion-paper, *ibid.* 337.

E. Vettchow (*Chem. Centr.* 1872, 361) has made a number of experiments on the sensibility of collodion as affected by the varying proportions of pyroxilin and iodising salts, from which it appears that, with the same amount of pyroxilin, a certain addition of iodising salts increases the sensibility of the collodion, but beyond this it rather diminishes this sensibility. The limit is  $1\frac{1}{2}$  per cent. of a solution containing 20 per cent. iodine and bromine, in the proportion of 3 parts iodine to 1 part bromine, added to collodion containing  $\frac{1}{4}$ ,  $\frac{1}{2}$ , or  $\frac{3}{4}$  per cent. pyroxilin.

The collodion should not contain less than about  $\frac{1}{2}$  per cent. of pyroxilin, nor should less than  $1$ – $1\frac{1}{2}$  per cent. iodine-solution, nor more than about 2 per cent. be added. The raw collodion should be made as thick as possible, and iodised so that the product may contain from 1.5 to 1.75 per cent. of iodine and bromine.

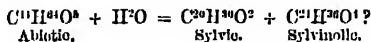
**COLOPHENE**. See OILS, VOLATILE.

**COLOPHONY**. This resin, usually regarded as a mixture of pinic, sylvic, and colopholic or pimic acid, consists, according to Maly (*Ann. Ch. Pharm.* cxxix. 94; cxxxii. 249; and *Gmelin's Handbook*, xviii. 2), chiefly of abietic anhydride  $C^{19}H^{32}O^4$ , together with a volatile oil. When the resin collected from pines or larches is freed from volatile oil by heating over the water-bath, there remains an amorphous yellow mass, which softens between  $90^\circ$  and  $100^\circ$ , is of a syrupy consistence at  $100^\circ$ , and dissolves easily in alcohol, ether, and chloroform; this body has the composition of abietic anhydride.

Abietic acid,  $C^{19}H^{30}O^3$ , is formed by the combination of the anhydride with water, and may be prepared by digesting powdered colophony for a week with alcohol of 70 p. c. whereby it is converted into a granular mass. By redissolving this mass in alcohol of 90 to 92 p. c., precipitating with hot water, and leaving the resinous precipitate to itself for one to three weeks, a crystalline mass is obtained mixed with a soft brown resin which may be removed by cold alcohol; and by pressing the remaining crystalline mass and recrystallising from hot alcohol, abietic acid is obtained in irregular, transparent, pointed crystals belonging to the triclinic system. It has an acid reaction, begins to melt at  $129^\circ$ , melts completely at  $144^\circ$ , dissolves in carbon bisulphide, wood-spirit, chloroform, alcohol, ether, and benzene. It is bibasic, forming mostly neutral salts; those of the alkali-metals are soluble in water and alcohol, and uncrystallisable. The neutral barium, calcium, and magnesium salts  $C^{19}H^{32}M^2O^4$  are amorphous precipitates, slightly soluble in water, easily in alcohol. An acid magnesium salt  $(C^{19}H^{30}O^3)_2Mg$  is obtained as a light white mass resembling magnesite, by boiling abietic acid with magnesium carbonate and pouring the filtered liquid into a large quantity of water. The silver salt,  $C^{19}H^{32}Ag^2O^4$ , is a white pulverulent mass, slightly soluble in alcohol, easily in aqueous ammonia and in ether. *Abietic acid*

$C^{14}H^{10}(C^2H^3)^2O^2$ , obtained by decomposing the silver salt with ethyl iodide, is a clear yellowish rather soft mass, becoming syrupy at  $100^\circ$ , decomposed by distillation, with elimination of water, insoluble in water, slightly soluble in alcohol, easily in ether and ether-alcohol. A mixture of concentrated alcoholic abietic acid and glycerin deposits, after standing for a fortnight, small white crystals of abietin, melting at  $125^\circ$ , and having, according to Maly, the composition  $C^{31}H^{70}O^3 = 3C^2H^3O^2 + C^{14}H^{10}O^2 - 6H^2O$ .

Abietic acid in alcoholic solution is decomposed by hydrochloric acid gas, producing sylvic and sylvinoic acids:



Sylvic acid is also produced when a hot alcoholic solution of abietic acid is mixed with sulphuric acid. Abietic acid triturated with phosphorus pentachloride yields on distillation, a volatile oil  $C^{14}H^{10}$  called by Maly, abietone, besides hydrochloric acid and phosphorus oxychloride. Fused with potash it yields propionic, but no pyroacetic acid. Sodium-amalgam added to a warm alcoholic solution of abietic acid converts it into the sodium salt of hydrabietic acid  $C^{14}H^{10}O^2$ . This acid forms white fatty laminae, melting completely at  $160^\circ$ : it is dibasic, forming neutral salts  $C^{14}H^{10}M^2O^2$  (Maly).

Strecker (*Ann. Ch. Pharm.* cl. 131; *Zeitschr. f. Chem.* [2] vi. 381) denies the existence of Maly's abietic acid, and regards the formula  $C^{14}H^{10}O^2$  as founded on incorrect analyses. He points out that the so-called abietic acid is prepared from the same material, and in the same manner, as the sylvic acid of Unvordorben, Trommsdorff, Siewert, and others (v. 611), Trommsdorff, and Siewert in particular, not having used sulphuric acid in the preparation, by which, according to Maly, abietic acid undergoes transformation; moreover, that the properties of abietic acid, as described by Maly, exhibit a general agreement with those of sylvic acid, excepting in the melting point, which has been stated by various authors at temperatures ranging between  $129^\circ$  and  $162^\circ$ . Duvernoy found  $139^\circ$ ; Maly's own statements, made at different times, vary between  $129^\circ$  and  $165^\circ$ . For these reasons, Strecker regards abietic acid as identical with sylvic acid, and as having the composition  $C^{20}H^{30}O^2$ . The same view is held by Duvernoy (*Ann. Ch. Pharm.* cxlviii. 143; *Zeitschr. f. Chem.* [2] v. 503). See, on the contrary, Maly (*Ann. Ch. Pharm.* cxlix. 244; *Zeitschr. f. Chem.* [2] v. 304; further *Ann. Ch. Pharm.* clxi. 1151).

In the last of these papers, Maly points out that Strecker's view of the identity of abietic and sylvic acids is founded chiefly on the experiments of Duvernoy, who obtained an acid having the composition  $C^{20}H^{30}O^2$ , not from ordinary colophony, but from French galipot, which is a very different material.

To throw further light on the question, Maly has repeated the preparation of the resin-acid from colophony in the following manner:—Coarsely pounded colophony is digested for two days with weak spirit, the liquid then poured off from the crystalline and nearly white pulp, and the latter squeezed in a press: if the residuo is not quite white, it may be rendered so by renewed stirring with alcohol, and pressure. A considerable quantity of the press-cake is dissolved in hot stronger alcohol, and the solution is left to itself either at ordinary temperatures, or in a cellar, whereby a white crystalline crust (1) is obtained, which slowly increases, and the mother-liquor when cooled by ice, usually solidifies to a pulp of loose white laminae (2) which constitutes the greater portion of the product. The former, especially when its quantity is small, gives by analysis numbers approximating to the formula of sylvic acid  $C^{20}H^{30}O^2$ , but the latter is found, both by combustion and by the analysis of its salts, to have the composition of abietic acid  $C^{14}H^{10}O^2$ . Great care is required in the analyses on account of the tendency both of the crystallised acids and of their salts to absorb oxygen from the air.

The abietates of the alkali-metals were found, as in the former investigation, to be uncrystallisable. The most definite is the sodium salt, which is obtained as a snow-white flocculent precipitate floating on the liquid, either by decomposing the potassium-salt with sodium nitrate, or by dissolving the acid in caustic soda and salting out with sodium nitrate. From this sodium salt the following salts were obtained, by double decomposition. The silver salt gave, as the mean of eleven determinations, 24.42 p.c. silver, the formula of the abietate,  $C^{14}H^{10}AgO^2$ , requiring 24.37, whereas that of the sylvate,  $C^{20}H^{30}AgO^2$ , requires 26.40. The barium salt gave somewhat variable results, ranging in fifteen determinations from 16.05 to 17.66 p.c. Ba; the abietate requires 16.98, the sylvate 18.54 p.c.\* The zinc salt gave 11.02 p.c. zinc oxide, which agrees exactly with the formula  $C^{14}H^{10}ZnO^2$ , whereas  $(C^{20}H^{30}O^2)_2Zn$  requires 12.14 p.c.

\* It is somewhat remarkable that some of the silver and barium salts analysed were prepared with acid of the first crystallisation, others with acid of the second crystallisation, and that nevertheless, all appear to have given analytical numbers agreeing most nearly with the formula  $C^{14}H^{10}O^2$ .

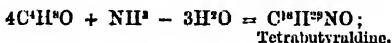
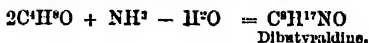
These results are regarded by Muly as confirming his former conclusion that the principal constituent of colophony is a resin-acid having the composition  $C^{14}H^{13}O_3$ ; it appears, however, to be mixed with a small quantity of another acid of different constitution, probably  $C^{20}H^{19}O_2$ .

Colophony oxidised with nitric acid yields chiefly isophthalic acid, together with trimellitic acid and a resinous acid (J. Schredor, *Deut. Chem. Ges. Ber.* vi. 413).

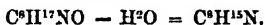
**COLUMBITE.** Syn. with NIOBITE; see TANTALATES.

**CONGLUTIN.** This name is applied by Ritthausen to the legumin of almonds and of lupines. (See LEGUMIN).

**CONINE.**  $C^8H^{15}N$ . *Artificial Formation* (Hugo Schiff, *Ann. Ch. Pharm.* clvii. 352. *Deut. Chem. Ges. Ber.* v. 42). When butyric aldehyde is acted upon by alcoholic ammonia at temperatures not above  $100^\circ$ , two bases, dibutyraldine,  $C^8H^{17}NO$ , and tetra-butyraldine,  $C^{16}H^{31}NO$ , are produced; the former by condensation of two, the latter by condensation of four molecules of butyraldehyde, with assumption of the elements of ammonia and elimination of water:



The former of these bases, when subjected to dry distillation, yields, among other products, a volatile, oily base, having the composition and many of the properties of conine from hemlock:



*Preparation.* 1. Butyric aldehyde heated for two months with alcoholic ammonia at about  $30^\circ$ , then for one day at  $100^\circ$ , afterwards neutralised with hydrochloric acid, and fractionally precipitated with platonic chloride, yielded a yellow flocculent precipitate of *tetra-butyraldine platinochloride*  $2(C^8H^{17}NO.HCl).PtCl^4$  forming the greater part of the product; and the mother-liquor gave by further treatment a small quantity of a yellow crystalline powder consisting of *dibutyraldine platinochloride*,  $2(C^8H^{17}NO.HCl).PtCl^4$ .

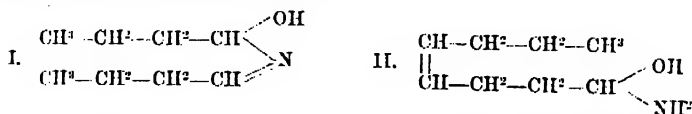
This last compound, decomposed with hydrogen sulphide and treated with concentrated potash-ley, yielded free dibutyraldine. On distilling this base with sand in an oil-bath, water and oily products passed over; and the distillate, freed from ammonia by gentle heating, neutralised with hydrochloric acid to separate tarry substances, concentrated, and mixed with platonic chloride, yielded a precipitate which by recrystallisation from alcohol, was obtained as an orange-coloured crystalline powder, having the composition of conine platinochloride  $2(C^8H^{15}N.HCl).PtCl^4$ . From this salt the base  $C^8H^{15}N$  was separated by means of potash and ether.

2. About half a kilogram of butyric aldehyde was mixed with an alcoholic solution of ammonia and placed in sunshine during the summer months; but, instead of neutralising with hydrochloric acid, and treating the solution with platonic chloride as above, the alcohol, ammonia, and unaltered butyric aldehyde were separated by distillation, the brown syrupy residue was heated for a day to  $130^\circ$ – $150^\circ$ , and the volatile portion distilled off in a current of steam. The tarry residue was then heated in sealed tubes to  $200^\circ$ , and again distilled with steam. On removing the basic portion of the oily distillate with hydrochloric acid, decomposing the resulting hydrochloride with potash, and repeatedly distilling the basic oil thereby separated in a stream of hydrogen, a portion boiling at  $166^\circ$ – $170^\circ$  was gradually obtained, then a second portion between  $175^\circ$  and  $195^\circ$ , and a third between  $205^\circ$  and  $215^\circ$ . The greater portion of the first fraction boiled at  $168^\circ$  and had the composition of conine.

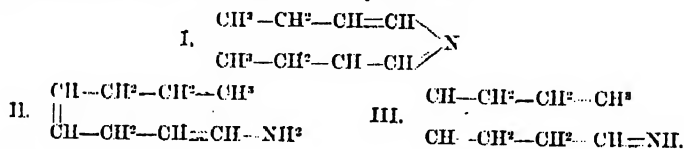
The base  $C^8H^{15}N$  obtained by either of these processes exhibits in the highest degree the odour of natural conine, and exerts a similar and equally violent poisonous action on the animal organism. It is very slightly soluble in water, the solution becoming milky when heated and clear again on cooling. Its solution, containing free hydrochloric acid, becomes light red when evaporated, afterwards violet, or, in presence of a strong hydrochloric acid, blue-green. When it is left to evaporate under a bell-jar over strong sulphuric acid, the acid acquires a deep red colour. Chlorine-water produces in the aqueous solution a white precipitate soluble in hydrochloric acid. Iodated potassium iodide produces a brown precipitate soluble in excess of potassium iodide. The base precipitates cupric hydrate from cupric sulphate, and silver oxide from the nitrate of silver. With mercuric chloride a thick yellow precipitate is formed, which unites into a viscid mass. A small quantity of the base introduced into a drop of auric chloride forms a viscid yellow precipitate which, in a few hours, becomes deep violet, yielding reduced gold.

All these reactions are exactly like those of natural conine; in the following reactions, however, differences are observed. Natural conine, evaporated with strong hydrochloric acid, acquires a deep indigo-blue colour; whereas the artificial base becomes only greenish-blue. The precipitation of silver oxide by natural conine at ordinary temperatures takes place immediately; artificial conino produces the same effect after some time only: immediately, however, at slightly higher temperatures (about 40°). The above-mentioned violet reaction with auric chloride takes place much more quickly with natural than with artificial conine. The platinumchloride of the artificial base is less soluble in water than that of natural conine. The artificial base differs also from natural conine in having a greater coefficient of expansion, in being less soluble in water, and in having no action on polarised light. The artificial variety is distinguished as *paraconine*.

To determine the constitution of conine and *paraconine*, the following considerations are adduced:—Dibutyraldine,  $C^8H^{12}NO$ , is susceptible of two isomeric modifications, according as the two aldehyde-residues which it contains are linked together by a nitrogen-atom or by carbon-atoms, viz.:



and these, by elimination of  $H^2O$ , give three isomeric conines, the first derived from butyraldine I., the second and third from butyraldine II.



Natural conine, which contains one atom of replaceable hydrogen (ii. 5), and in which the group  $C^4H^4$  (conylene) is bivalent (ii. 964) is represented by the third formula. Artificial conine contains no replaceable hydrogen, inasmuch as no separation of water occurs on heating it with ananthol; and when treated with ethyl iodide, it yields the iodide of an ammonium base, the oxide of which is a bitter, alkaline, easily decomposable syrupy liquid; its constitution may therefore be represented by the formula I.

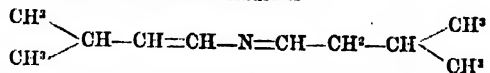
Other isomerides of conino may perhaps be formed from isobutyric aldehyde, or from a mixture of this with normal butyric aldehyde.

The portion of the oily distillate obtained in the second mode of preparing *paraconine* (p. 380) which boils above 200°, contains the base  $C^{10}H^{12}N$ , derived from tetrabutryaldine. This base is formed also in small quantity by the distillation of *paraconine*: thus—



It boils at 210°, and has a specific gravity of 0.915 at 15°.

The base  $C^{10}H^{12}N$  obtained by Ljubavon from valerinaldehyde is doubtless the 10-carbon *paraconine*. Its constitutional formula is—



Optically active valerinaldehyde would probably yield the corresponding homologue of natural conine (Schiff).

**CONNECTIVE TISSUE.** It is not yet definitely ascertained in how far the connective tissue of the invertebrata agrees with that of the vertebrata, or in how far it is to be considered as true embryonal tissue. Microscopical investigation has shown that the connective tissue of invertebrata mostly corresponds in appearance with the connective tissue of the vertebrates. Only in some groups is mucous tissue found (*Calenterata*, *Vermes*, *Heteropoda*), while the fibrillar tissue is found only in the *Cephalopoda*, cartilage only in the *Cephalopoda* and in the lingual cartilage of the *Gasteropoda*, while bone does not exist in the invertebrata at all. The question to determine was whether all these tissues really agree with their homologues in the vertebrata in chemical composition, and whether gelatin might be obtained from them.

A number of vineyard snails were boiled for some time. The decoction did not gelatinise. It was completely precipitated by acetic acid, and hence must be regarded

as chondrin, or some similar substance. It could be converted into chondro-glucose by boiling with hydrochloric acid. A similar result was obtained with fresh specimens of *Anodonta* and *Unio*.

The *Gastropoda* and *Lamellibranchiata* therefore possess a connective tissue nearly allied to the connective tissue of vertebrates. They differ, however, from the *Cephalopoda*, for Hoppe-Seyler obtained from these, specimens of pure gelatin free from chondrin.

To determine whether the pen of the *Sepiæ* and *Loligidæ* contained a substratum of connective tissue, the salts were dissolved out by hydrochloric acid, and the framework boiled in closed tubes for twenty hours. The decoction did not gelatinise, but became turbid when cold. This substance was insoluble in alcohol, but soluble in acetic acid and sodium acetate. Ferro-cyanide of potassium caused no precipitate. The other characters show that the stroma of the sepiæ-pen is not conchiolin, as might have been supposed from its homology with the shells of molluscs. It would appear that in the cephalopods the chitin of the arthropods and the connective tissue of the vertebrates are combined. No gelatin or similar substance could be obtained from cockchafer, which were under analysis for chitin (Frerich, *Pflüger's Archiv. f. Physiologie*, 1872, 320).

**COPPER.** A specimen of supposed native copper found in a cargo of copper pyrites from the Tharsis mines in Spain is described by H. Bowman (*Chem. News*, xxiii. 19). It weighs 2½ lbs., has a specific gravity of 8·4, and varies in colour in different parts from copper-red to almost white, with a hackly fracture. The interior is full of cavities above shot size. Its composition is:

Cu	Fe	Zn	Ni	Co	Sb.	As.	S.	O.
84·80	5·54	trace	0·78	0·14	0·50	7·10	0·73	0·41 = 99·50

On the occurrence of copper in Cajuput oil, see page 231.

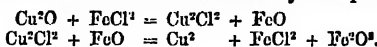
*Selenium in Copper.* According to Violette (*Compt. rend.* lxx. 729), commercial copper sometimes contains selenium. To separate this element, the metal is first oxidised in a muffle-furnace, and the oxide thus formed is heated to redness for several hours in a stream of pure dry air. If the copper contains selenium, there is found after some time at the end of the tube, a white volatile crystalline ring which exhibits all the reactions of selenious acid. In this manner the selenium may be not only detected, but estimated.

*Alloys of Copper with Cobalt and Manganese.* With cobalt, copper forms ductile and malleable alloys which fuse at about the melting point of copper. Manganese has a great affinity for copper. Alloys containing 3, 5, 8, 12, 15, and 20 p.c. manganese have been prepared; they all greatly resemble the alloys of copper and tin, are very hard and sonorous, and fuse readily. The alloy containing 15 p.c. manganese is grey, very hard and brittle, melts like bronze, may be readily cast, and does not appear to alter by keeping. The 12 p.c. alloy is still brittle; it is grey after rolling, but soon acquires a brass-yellow colour. The alloys containing less manganese are ductile, and may be hammered out into plates as thin as brass-foil (Valenciennes, *Compt. rend.* lxx. 319).

*Electrodeposition of Copper and Brass.* A solution containing one pound of cupric sulphate and one pound of sulphuric acid to the gallon of water, deposits the metal in a solid compact mass, with a somewhat botryoidal surface. The addition of one ounce of zinc sulphate (as recommended by Napier) annuls this botryoidal form, and renders the deposit tough, compact, and even. From a solution containing a greater proportion of zinc sulphate the metal is deposited in tufts of needles standing at right angles to the surface of the metal. Ordinary electro-brassing solutions show the same peculiarity in even a more marked degree, and this makes it impossible to produce a good deposit of more than 0·01 to 0·03 inch in thickness. This form of deposit is owing chiefly to a copious evolution of hydrogen taking place during its formation. But, by employing a solution containing both the oxides and the cyanides of the constituent metals, together with some neutral ammonium tartrate, this evolution of hydrogen may usually be avoided, or, should it, nevertheless, take place to a slight extent, it may be entirely stopped by the addition of cupric ammonide. Such a solution yields brass of a uniform character, and the deposit, which may be obtained of any desired thickness, is tough, and has a compact even texture. As there is no evolution of hydrogen, no electric force is wasted, and perfect results may be obtained with a single Wollaston's or Smee's cell (W. H. Waller, *Phil. Mag.* [4] xli. 41).

**Absorption of Gases by Electro-deposited Copper** (R. Lenz, *J. pr. Chem.* cviii. 438).—Copper precipitated by electrolysis from a solution of cupric sulphate contains a certain quantity of gases which escape on ignition. Taking the volume of the copper = 1, the composition of the gaseous mixture in volumes per cent. is found to be 77.3 hydrogen, 8.4 carbon oxide, 11.1 carbon dioxide, and 3.2 water-vapour.

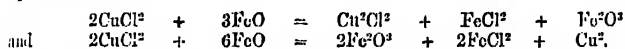
**Reactions of Copper-compounds.** Cuprous oxide dissolves in a strong solution of magnesium chloride even in the cold, more easily, however, at the boiling heat, with separation of magnesium hydrate and formation of cuprous chloride. Cuprous and ferrous oxide and chloride in the manner as shown by the equations:



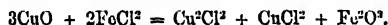
The final result of the action of cuprous oxide on ferrous chloride may be represented by the equation:



The reaction between cupric chloride and ferrous oxide is represented by the equations:



Cupric oxide is decomposed by ferrous chloride in the following manner:



The insolubility of the cuprous chloride renders the action very slow; but if common salt be added, and the liquid heated so as to increase the solubility of the cuprous chloride, the transformation is rapid and complete (T. Sterry-Hunt, *Compt. rend.* lxi. 1357).

Aluminium immersed in a solution of cupric sulphate or nitrate does not act upon it at first, but after two days, the foil becomes covered with crystals consisting partly of dendrites, but for the most part of well-defined octahedrons. A solution of the nitrate yields, together with metallic copper, a green insoluble powder consisting of a basic salt. Copper is immediately precipitated by aluminium from a solution of cupric chloride, and likewise, though more slowly, from the acetate. The reduction also takes place immediately when to the solution of the sulphate or nitrate there is added a small quantity of a very dilute solution of an alkaline chloride, the precipitation being complete if a sufficient quantity of aluminium is present (Cossa, *Il nuovo Cimento* [2] iii. 75).

**Detection of Copper.** According to F. Bellamy (*Zeitschr. anal. Chem.* ix. 382), a five-millionth part of copper or iron may be detected in water by the blue colour produced by addition of an alcoholic extract of logwood, whereas the bicarbonates of the alkalis or alkaline earths merely change the yellow colour of the tincture to a light reddish violet. An excess of hæmatoxylin gives rise to the formation of blue flocks, which may be further examined for copper or iron.

Schönbein observed (*ibid.* viii. 67), that nearly all copper salts, in presence of hydrocyanic acid, impart to solutions of guaiacum, and to starch-paste containing potassium iodide, a deep blue colour. Brown cupric cyanide and green cuproso-cupric cyanide produce this reaction even in very dilute solutions. Further, it is found by E. Schar (*ibid.* ix. 93 and 109), that cupric cyanate, sulphocyanate, and ferricyanide also possess this property, whereas cupric ferrocyanide acts only on guaiacum, not on potassium iodide. All soluble cyanides, ferrocyanides, ferricyanides, sulphocyanates, and nitroprussides are capable of indicating the presence of traces of cupric salts by the blueing of guaiacum. A solution containing only  $\frac{1}{1000}$  p.c. of cupric sulphate is still coloured very distinctly blue by the addition of a little prussic acid and tincture of guaiacum. In carrying out this mode of detection, A. Aë (*ibid.* ix. 901) recommends the addition of a few drops of chloroform to the mixture, which is to be gently agitated and left to stand. The chloroform then acquires a deep blue colour, even if the dilution is so great that no change of colour is perceptible in the aqueous liquid.

**Quantitative Estimation.** At the Mansfeld copper works, the quantity of copper in poor ores and schists was formerly estimated by Rose's method, as cuprous sulphide (1st *Suppl.* 492), and in the richer reguli (*Rohsteine* and *Spursteine*), by the Swedish method of precipitation with metallic iron. Both these methods, however, require too much time to be available for the metallurgic assaying. The Directors, therefore, in 1807, offered a prize for the discovery of a process which could be completed in five or six hours, and should yield results lying between fixed limits of error. Out of sixteen essays, the prize was adjudged to only one, namely that of

Steinbeck, as fulfilling all the required conditions; but honourable mention was also made of a second, by C. Luckow, for its simplicity, cheapness and elegance.

1. Steinbeck digests 5 grams of the finely pulverised schist with 40 to 50 c. c. of common hydrochloric acid of sp. gr. 1.16; allows the carbonic anhydride to escape; and adds to all bituminous ores, 6 c. c. of a mixture of equal volumes of water and pure nitric acid of sp. gr. 1.2, to non-bituminous or previously roasted ores, only 1 c. c. After half an hour's digestion, the liquid is boiled briskly for ten to fifteen minutes, whereby the whole of the copper is dissolved, together with the other metals present (the residue being found to contain not more than 0.03 p.c. copper), and all the nitric acid together with lower oxides of nitrogen is driven off. The solution is filtered into a beaker-glass, in which is placed, upon a strip of platinum foil, a bar of zinc as free as possible from lead, weighing about 8 grams. In half or three-quarters of an hour the whole of the copper is precipitated; the excess of zinc is then removed, and the spongy metallic precipitate is washed by decantation with spring water. This precipitate is treated with 8 to 16 c. c., according to its quantity, of the above-mentioned nitric acid mixture, and dissolved at a gentle heat; the solution, after cooling, is mixed with 10 c. c. of a mixture of 2 vols. water and 1 vol. ammonia of sp. gr. 0.93 (if 16 c. c. of nitric acid have been used, the liquid must be previously diluted to 100 c. c., and halved with a pipette). The next step is the titration of the copper with solution of potassium cyanide (il. 58), 1 c. c. of which indicates 0.005 gram of copper, so that as 5 grams of substance were taken for the assay, 1 c. c. indicates 0.1 p.c. copper. The termination of the experiment is indicated by the complete disappearance of the blue colour. With constant use the change in the strength of the standard solution is inconsiderable; indeed, it need not be redetermined more than once a week, as the alteration is barely perceptible even in a fortnight. By the preceding process six samples of ore may easily be assayed in four hours.

When the directions above given are closely observed, the variations in the amount of ammonium nitrate, free ammonia, lead, and zinc in the liquid to be assayed, do not affect the final result by more than 0.05 p.c. Greater variations may arise from performing the titration at a higher temperature, on which account the ammoniacal copper solution must be previously cooled.

2. Luckow precipitates the copper electrolytically. He finds that even proportionately weak voltaic currents are capable of precipitating copper in beautiful reguline form from solutions not containing more than 0.1 gram nitric acid in the cubic centimeter (nitric acid of sp. gr. 1.2 contains 0.32 gram in the cubic centimeter). From the acid solution the following metals are not precipitated by the current: zinc, iron, nickel, cobalt, chromium, the earth-metals, alkaline earth-metals and alkali-metals. On the other hand, lead and manganese are completely precipitated at the positive pole as peroxides, silver only partially; easily oxidisable substances, organic or inorganic, ferrous oxide, for example, retard the precipitation at the negative pole, mercury, silver, copper and bismuth are deposited in reguline form, the mercury first, which afterwards forms an amalgam with the copper. From arsenic and antimonie acids, arsenic and antimony are separated some time after the precipitation of the copper.

In the application of this method for assaying purposes, the copper schist (2 grams) is first roasted, with stirring, for six or seven minutes on an iron crucible cover or in small porcelain crucibles. The roasted product is introduced by means of a bent card into a small beaker glass, washed off the sides of the glass with 2 or 3 c. c. of nitric acid, sp. gr. 1.2, and mixed with 10 to 15 drops of strong sulphuric acid. The whole is then gradually heated on a sand-bath, and at last strongly enough to drive off all the sulphuric acid. To prevent spitting, the liquid is covered with a perforated watch-glass (or a wide-necked funnel). The evaporation may be accelerated by addition of 10 to 20 drops of hydrochloric acid, but even then it takes from an hour to an hour and a half. When the liquid has cooled, the watch-glass (or funnel) is rinsed with nitric acid of sp. gr. 1.2 diluted with 6 vol. water, the beaker is filled to one-half with the same liquid, and a few drops of tartaric acid are added. For the precipitation of the copper, a platinum wire half a line thick,  $7\frac{1}{2}$  inches long and rolled up for  $\frac{2}{3}$  of its length into a flat spiral like a watch-spring is used as the positive pole. If the liquid above the evaporation-residue is very turbid, 1 or 2 c. c. of a strong solution of barium nitrate is added, and mixed with the liquid by moving the spiral up and down. The acid liquid, after standing for a while, remains only slightly turbid. The negative pole is formed of a cylinder of platinum foil  $2\frac{1}{2}$  inches long,  $1\frac{1}{2}$  inch broad, and immersed in the liquid to three-fourths of its length, so that it remains separated from the spiral by about  $1\frac{1}{2}$  line. The circuit being now closed, the termination of the copper precipitation is easily ascertained by immersing the platinum cylinder deeper in the liquid, after addition of dilute sulphuric



and observing whether any further deposition of copper takes place on the clean part; if the battery is sufficiently strong, the precipitation is usually completed in about eight hours. The increase of weight of the platinum foil, after washing with water, rinsing with alcohol and drying, gives the quantity of copper present. For the assaying of poor ores, the current should be capable of evolving from 16 to 25 c. c. of detonating gas in half an hour; for richer ores and reguli (containing more than 60 p.c. copper) a current is required capable of evolving from 50 to 75 c. c. of detonating gas in the same time. Silver must be removed with very dilute hydrochloric acid, the liquid made up to 200 c. c., and the washing of the copper in the beaker effected by displacing the mother-liquor with a stream of water.

Further details of this method, especially with reference to the assaying of rich ores and reguli, and such as contain considerable quantities of iron are given in the *Zeitschrift für Analytische Chemie* xi. Jahrgang, 1-16. In ores containing from 17 to 21 p.c. iron difficulties arise from the action of nitrogen dioxide or ferrous oxide, which takes place simultaneously with the reduction of the copper at the negative pole, the metallic solution acquiring a brown-black colour, which increases as the precipitation of the copper goes on, especially outside the platinum cylinder, where the action of oxygen is but slight, whereas within the cylinder, where oxygen is evolved in excess, no such coloration takes place. This coloration is avoided by using for the negative electrode, instead of the cylinder, a hollow cone of platinum having several slits in its side. A negative electrode of this form, not only prevents loss by the spitting of the oxygen-bubbles, but likewise allows the oxygen evolved at the inner surface of the cone to escape through the slits to the outer side, whereby the partial reduction of the ferric to ferrous oxide, and of the free nitric acid to nitrogen dioxide, and consequently the black-brown coloration of the liquid, is prevented. For highly ferruginous samples, the current must be strong enough to yield from 100 to 120 c. c. of detonating gas in half an hour.

The copper precipitated as above described is often covered with a brown or black film of some foreign substance, which, when the quantity of copper is small, may render the result of the analysis inexact. The quantity of this black deposit is too small to allow of the determination of its nature by analysis; but synthetical experiments have shown that arsenic and selenium are separated by the electric current, but later than the copper, which therefore becomes coated with those substances. Antimony and bismuth have not been detected in the schists and furnace-products of Mausfeld. It has lately been found that selenium may be completely precipitated by the electric current from nitric acid solutions. In many cases, however, the grey-black colorations of the copper appear to owe their origin to traces of hydrochloric acid in the solution: indeed they are produced by the addition of extremely small quantities of this acid.

The whole of the lead contained in the solution mostly separates as peroxide on the spiral which forms the positive pole, and must be estimated gravimetrically, if its quantity is not great. When larger quantities are present, part attaches itself to the platinum wire and the rest separates in the form of loose thin laminae. Experiments are still in progress, for the purpose of discovering an exact method of estimating the lead.

To render the electrolytic determination of copper generally applicable, it is very desirable to get rid of the black deposits above mentioned. As they make their appearance only after the precipitation of the copper, this end might perhaps be attained by stopping the process as soon as the black deposits begin to show themselves; but it would be difficult to ensure that the whole of the copper had been precipitated. By the following method, however, the desired certainty may be attained. As soon as the precipitation is completed, the hollow platinum cone, together with the black copper deposit, is removed in the ordinary way from the glass, then rinsed, dried, and gently ignited for a short time in a gas or spirit flame or in a red-hot muffle. The dark substance then volatilises, and the metallic copper is converted into cuprous or cupric oxide without perceptible loss. The cylinder or cone thus treated is placed in a small beaker glass, and connected with the conducting wire proceeding from the positive pole of a small battery; and a somewhat larger, previously weighed platinum cylinder attached to the wire proceeding from the negative pole of the battery, is suspended over it. On pouring into the glass a sufficient quantity of dilute nitric acid (1 acid to 6 water) or an equivalent quantity of 1:8 dilute sulphuric acid, the electrolytic action begins. The oxidised copper attached to the cylinder which serves as positive pole, dissolves, and is deposited with bright metallic lustre on the cylinder which serves as negative pole. The entire manipulation takes a few hours longer than the preceding process, but it yields good results.

This process is applicable, however, only when the quantity of antimony, arsenic or selenium present is very small; in that case the platinum is not attacked, because the black deposit is formed on the copper alone. But when larger quantities of these

substances are present, the only thing to be done is to watch for the moment when the precipitation of the copper is completed, and it begins to blacken. The current must then be interrupted, and the platinum cone taken out of the solution and treated as above.

In the assay of highly ferruginous copper ores, &c., the addition of oxalic acid to the liquid is recommended instead of tartaric acid.

As already observed, the strength of the current must be varied according to the quantity of copper present in the assay, large or small batteries being used accordingly. The paper above cited in the eleventh volume of the *Analytische Zeitschrift* gives a full description of the forms of battery which have been found best adapted for the purpose. With the apparatus there described, it is said that two persons can make 10,800 copper determinations in a year.

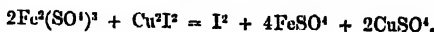
On the electrolytic precipitation of copper see also Merrick (*Chemical News*, xvi, 155, and Lecoq de Boisbaudran, *Bull. Soc. Chim.* [2] vii, 468; xi, 35; *Jahresb.*, 1867, 850; 1869, 901).

*Estimation by Precipitation as Sulphide, Iodide, and Sulphocyanate* (1st Suppl. 492). According to Ulrici (*J. pr. Chem.* cvii, 110) the weight of copper sulphide precipitated by hydrogen sulphide and ignited, bears a constant ratio to that of the copper contained in it. The residue left on ignition is always a mixture of cuprous sulphide and cupric oxide, though its weight corresponds almost exactly with the formula  $\text{Cu}_2\text{S}$ . By ignition in an open crucible more oxide is formed and less sulphide, whereas in a covered crucible, which, however, must be removed from the flame from time to time and opened for a few seconds, a residue is obtained, represented in composition by the formula  $\text{Cu}_2\text{S} \cdot \text{CuO}$ . As, however, the percentage of copper in the sulphide  $\text{Cu}_2\text{S}$  is the same as that in the oxide  $\text{CuO}$ , it matters not, so far as the calculation of the amount of copper is concerned, in what proportion these two compounds are mixed. An excess of sulphur precipitated together with the copper sulphide, has of course no influence on the result. By a series of seventeen experiments in which copper was dissolved in nitric acid, and precipitated, after dilution, with hydrogen sulphide, it was found that, on igniting the strongly dried precipitate in an open crucible, residues were obtained which gave by calculation from 100.9 to 102.6 p.c. copper, whereas experiments in a covered crucible gave from 99.8 to 100.8 p.c. As the differences are perhaps attributable to the ashes of the filters, and the results of half the experiments did not differ from the calculated quantity by more than 0.2 p.c., this simplified process appears to be capable of yielding good results.

According to E. Fleischer (*Chem. News*, xix, 206) the precipitation of copper as sulphide by heating a solution of cupric chloride with sodium thiosulphate is well adapted for the separation of copper from metals whose sulphides are soluble in dilute hydrochloric acid. The precipitate contains excess of sulphur, and cannot, therefore, be directly dried and weighed. It might, however, be treated by Ulrici's method just described.

According to Duclaux (*Bull. Soc. Chim.* [2] xviii.; *Chem. News*, xxv, 156), very small quantities of copper may be estimated by precipitation with hydrogen sulphide, redissolving the sulphide in a platinum crucible, reducing the copper with zinc in contact with the platinum, then washing out the crucible with alcohol, drying, and igniting it together with the copper deposit. In this manner, Duclaux states that he has found in 1000 parts of the ash of cæno-beans, from 0.009 to 0.040 part of copper; in 1000 parts of the outer shell, from 0.035 to 0.225 of copper, and in chocolate from various makers from 0.005 to 0.125 part.

For the transformation of cupric salts into cuprous iodide, the only advantageous reducing agent is according to Fleischer, *stannous chloride*, since both sulphurous acid and ferrous chloride dissolve considerable quantities of cuprous iodide. Addition of sal-ammoniac facilitates the precipitation, which, if the liquid be kept cool, is so complete that no copper can be detected in the filtrate by potassium ferrocyanide, or by introducing a platinum wire wetted with it into a colourless flame. The cuprous iodide after washing with solution of sal-ammoniac (if washed with pure water it passes through the filter) is warmed with a solution of ferric sulphate, whereupon the following reaction takes place:



The separated iodine may be completely expelled by boiling for ten minutes, and the ferrous oxide estimated by permanganate, every 2 molecules of it corresponding to 3 atoms of copper. This method may also be used for the estimation of iodine in presence of chlorine and bromine.

The precipitation of copper as cuprous sulphocyanate,  $\text{Cu}_2(\text{ONS})^2$ , recommended by Rivot is performed by Fleischer as follows: The cupric chloride or sulphate

addition of potassium or sodium chloride, is reduced, if free from iron, with sodium sulphite, in the contrary case, with stannous chloride, after which potassium sulphocyanate and sal-ammoniac are added. The washed precipitate is boiled with caustic potash or soda, and the cuprous oxide thereby produced is quickly separated by filtration and titrated as above with ferric sulphate.

*By Titration with Potassium Ferrocyanide.*—Galetti (*Bull. Soc. Chim.* [2] ii. 83; *Zeitschr. anal. Chem.* viii. 135; *Jahresh.* 1864, 710; 1869, 901), uses for this purpose a solution containing 32.485 grams of ferrocyanide in the litre, so that 100 c. c. correspond with 1 gram of copper, according to the equation  $K^+FeCy^{4-} + 2CuCl^+ = 4KCl + Cu^2FeCy^4$ . To apply this method to the analysis of copper pyrites, the mineral is first oxidised with strong nitric acid, hydrochloric acid is then added, the solution evaporated to half its bulk, then diluted and mixed with ammonia in quantity rather more than sufficient to precipitate the whole of the iron. It is then boiled with a quantity of acetic acid sufficient to give it an emerald-green colour; ammonia is again added in excess, and the liquid is acidulated with very dilute acetic acid. As soon as the basic ferric acetate has settled down, the copper is precipitated by potassium ferrocyanide. The liquid may also be filtered after the second addition of ammonia, and the precipitate washed with a boiling dilute solution of acid ammonium acetate (20 grams of acetic acid saturated with ammonia and then mixed with 15 grams of acetic acid and 585 of water). If zinc, nickel, or cobalt is present, the copper must first be precipitated as sulphide or in the metallic state, then redissolved and treated as above.

*By Titration with Potassium Cyanide.*—In applying this method, described in vol. ii. p. 58, to the estimation of copper in compounds containing zinc, some modification is required to counteract the disturbing influence of the zinc. Yvon (*Compt. rend.* lxxiv. 1252) proceeds as follows: Solutions of zinc and copper nitrates, with excess of ammonia, containing 1 gram of metal per litre, are first prepared. The amount of cyanide required to decolorise 50 c. c. of pure copper solution is noted, and then the amounts after addition of 5, 10, 15, 20, &c., c. c. of zinc solution. From these results the amounts corresponding with 1 c. c. of cyanide are deduced.

The alloy to be analysed, such as brass, is dissolved in nitric acid, ammonia added, and the whole made up to a litre. After titrating 50 c. c. with cyanide, another 50 c. c. is acidified strongly, boiled with sodium thiosulphate, and the cupric sulphide dissolved in nitric acid and ammonia, and again titrated. The difference represents the zinc.

On the determination of copper in brass by titration, see also Kirpitschon (*Zeitschr. f. Chem.* [2] vii. 207; *Chem. Soc. J.* [2] ix. 755).

*By Titration with Stannous Chloride.*—F. Weil (*Ann. Ch. Phys.* [4] xxv. 109) describes this method as based on the two facts, (1.) That in a hot solution containing excess of hydrochloric acid, the least trace of cupric chloride gives a greenish colour, the tint being deeper as the quantity of acid is larger. (2.) Stannous chloride instantly reduces green cupric chloride to colourless cuprous chloride.

A solution of stannous chloride containing 6 grams of tin per litre is titrated with a solution of cupric sulphate containing 4 grams of copper per litre; 25 c. c. of this solution are treated with 10 c. c. of concentrated hydrochloric acid, and heated to boiling, and the tin solution is rapidly added till the liquid becomes colourless; 10 c. c. more acid are now added, and if the liquid acquires thereby a greenish tint, tin-solution is slowly dropped in till no colour remains. To make quite sure that the tin-solution is in slight excess, 1 c. c. of the cooled liquor is treated with a drop of saturated solution of mercuric chloride; 0.05 c. c. of the tin-solution in 30 c. c. of liquid causes a distinct turbidity of calomel when thus treated. This volume is therefore deducted from the total volume of tin-solution used, and the strength calculated from the remainder.

*Estimation of the Copper.*—1. *When Iron and Nickel are absent.*—The substance is heated with strong nitric acid; the nitric acid is expelled by sulphuric, or in the case of silver, by hydrochloric acid; the volume of the solution is brought to 250 c. c. or 500 c. c.; 25 c. c. are then treated with the tin-solution exactly as above described in the case of the standard copper-solution, and the quantity of copper present is calculated from the volume of liquid employed.

2. *When Iron is present.*—*Process A.* 25 c. c. of the solution to be tested are reduced as just described. A fresh quantity of the same volume is then heated with water, metallic zinc, and platinum-foil till all the iron is reduced. The copper, together with any lead, tin, or arsenic that may be present is thus precipitated as metal. The iron is then estimated in the decanted liquid with permanganate. The strength of the tin-solution having been calculated for iron from the number for copper, the proper deduction is made from the total quantity used. *Process B.* The metallic copper precipitated as described under *A* may be dissolved and directly

estimated with tin-solution without estimating the iron. *Process C.* The solution containing ferrous salt, described in A, may be treated with permanganate till the latter is in distinct excess, then boiled till no red colour remains but that due to iron. Tin-solution is now added till the iron is reduced, and the quantity thus used is subtracted from the total quantity employed for copper and iron together.

3. *When Nickel or Cobalt is present.*—*Process A.* The solution of the substance in nitric acid or aqua regia is nearly neutralised with sodium carbonate and then agitated with barium carbonate till all the copper and iron are precipitated. The precipitate is dissolved in acid, and the copper in it is estimated by tin-solution. *Process B.* See above, 2nd Application, B.

Arsenic does not interfere with this method, since arsenic acid is not reduced by stannous or cuprous chloride. The results obtained vary only a few tenths of a per cent. from those obtained in the gravimetric way.

*Separation of Copper from Bismuth.*—The separation of these metals when they are alloyed together may be effected by treating the alloy at a low red heat with potassium sulphocyanate. One part of a mixture of 8 parts potassium cyanide and 3 parts of sulphur is thrown upon 16 parts of the alloy melted at a low temperature. As soon as the reaction takes place, the crucible is covered, and when all deflagration has ceased, the metal is well stirred with a clay rod, the flux allowed to set, and the fluid metal poured out. The bismuth thus obtained is quite free from copper (H. Tamm. *Chem. News*, xxv. 85).

*Separation from Silver.*—A quick method of separating these metals is based on the fact that silver nitrate is insoluble in strong nitric acid, whereas cupric nitrate is soluble. The nitric acid solution of the metals is evaporated to the consistence of a thick oil, and then mixed with strong nitric acid free from hydrochloric acid, whereby all the silver salt is precipitated in the crystalline state, the copper salt remaining in solution. The precipitate, which is coloured blue from adhering copper salt, is obtained quite white and free from copper by two or three washings with strong nitric acid. The adhering acid evaporates on drying the precipitate. Care must be taken not to evaporate the mixed nitrate solution to dryness, as it is then very difficult to wash out the copper from the precipitated silver nitrate. The more concentrated the nitric acid, the more fully is the silver salt thrown down. An acid of sp. gr. 1.25 gives good results. For every part of concentrated metallic solution, three to four parts of acid are requisite for separation. R. Palm (*Dingl. polyt. J.* cciv. 75).

According to Hahn (*Chem. Centr.* 1870, 240; *Zeitschr. f. Chem.* vi. 352) the separation of copper from silver cannot be effected by dissolving the two metals in excess of potassium cyanide and treating the solution with hydrogen sulphide or the sulphide of an alkali-metal—whereby, according to Rose and Frosenius, the silver is precipitated as sulphide, while the copper remains dissolved—inasmuch as the sulphides of both these metals are soluble in potassium cyanide, and only mercury, if present, is thrown down as sulphide.

#### Compounds of Copper.

**Arsenide.**—Frenzel (*Jahrbuch f. Mineralogie*, 1873, 26), has examined three varieties of this compound, regarded by mineral dealers as distinct species, and named accordingly. I. Domeykite from the San Antonio mine near Copiapo, Chile. II. Algodonite from Lake Superior. III. Whitneyite from Cerro las Paracutas, Cigazuala, Mexico. Analysis showed that all three are varieties of one species, Domeykite, viz. :—

Sp. gr. (at 22°)	I.	II.	III.
	6.700	7.207	7.547
Copper	70.16	72.02	72.99
Arsenic	25.89	28.29	27.10
Iron	3.50	—	—
Manganese		—	—
Sulphur	0.49	—	—
Residue	0.45	—	—
	100.49	100.31	100.09

The formula of Domeykite,  $\text{Cu}_2\text{As}$ , requires 71.72 p.c. copper and 28.28 arsenic. The 25.88 p.c. of arsenic found in I. would require, according to this formula, 55.94 p.c. copper. The copper arsenide in it is probably mixed with native copper, iron arsenide, and a sulphur compound. The third variety also probably contains native copper.

All three varieties exhibit, on newly fractured surfaces, a tin-white to bluish

colour. The bright metallic lustrous powder of II. (the purest variety) is light grey; that of III. dark grey; of I. greyish black. In the course of 24 hours they all acquire a yellow tarnish.

Accompanying these minerals were found native copper, red copper ore, malachite, quartz, and small quantities of a radio-fibrous mineral, probably wavelite.

Weisbach (*ibid.* 64) describes a variety of Domeykite found imbedded in the argillaceous porphyry (*Thonsteinsporphyr*) on the right bank of the Mulde, near Zwickau. It occurs in masses having a dense or very fine-grained fracture, with a decided tendency to cleavage, and therefore to crystalline structure. Colour and streak blackish grey. Lustre metallic, brighter on the streak. Hardness 5 (equal to that of apatite). Sp. gr., 6.84. Brittle, with decided inclination to softness. It differs from the Chilian mineral chiefly in colour and hardness, the latter being tin-white, and intermediate in hardness between calcspar and fluor-spar. This Zwickau mineral affords the first instance of the occurrence of Domeykite on the continent of Europe.

**Chlorides.**—According to Maumond (*Chem. News*, xxv. 156), when cuprous chloride is formed by the gradual combination of copper with chlorine, an external layer of cupric chloride is produced at the same time, and these two chlorides unite together forming the compound  $\text{Cu}^+\text{Cl}^{10} = 3\text{CuCl}^2 + 2\text{Cu}^2\text{Cl}^2$ .

**Iodides.**—*Cuprous iodide*,  $\text{Cu}^+\text{I}^2$ , is formed by the action of copper on hydriodic acid. When strips of copper or pieces of copper-wire are immersed in this acid, no formation of iodide takes place as long as the liquid remains colourless; but as soon as iodine begins to separate, pulverulent cuprous iodide is also precipitated, and the reaction once commenced goes on quickly. By retarding the separation of iodide, which may be effected by the introduction of traces of hydrogen sulphide, the cuprous iodide may be obtained in tetrahedral crystals. Larger and better developed tetrahedrons, sometimes with combination-faces, are produced by the action of hydriodic acid on cuprous sulphides, as, for example, on the slightly oxidised copper-glance of Sangerhausen. The crystals have a greenish yellow colour, becoming darker on exposure to light (E. Miesel, *Dent. Chem. Ges. Ber.* iii. 502).

Cuprous iodide is also formed, together with allyl bromide, by the action of allyl iodide on an alcoholic solution by cupric bromide (Oppenheim, *ibid.* 412).



**Cuproso-mercuric Iodide.**— $\text{Cu}^+\text{HgI}^4$ . When cupric sulphate is added to a boiling solution of potassio-mercuric iodide, a large quantity of iodine is set free, and cuproso-mercuric iodide is precipitated as a dark brown powder changing on cooling to a fine red. When heated either alone or with water, it becomes dark-coloured, but recovers its red colour on cooling. According to Miesel (*Berliner Monatsberichte*, 1870, 123), this precipitate is a mixture of cuprous and mercuric iodides; but Wilm and Caventou (*Bull. Soc. Chim.* [2] xiii, 220) regard it as a definite compound, because when cold it has a deeper red colour than mercuric iodide, and it is but very slowly decomposed in the cold by potassium iodide, whereas mercuric iodide, as is well known, is quickly dissolved by that reagent. On heating the precipitate with potassium iodide, mercuric iodide is dissolved and cuprous iodide remains. With ammonia, the double iodide yields two kinds of crystals, both containing mercury and copper. Boiled with ammonia, it yields a blue solution, and a very heavy brown liquid which solidifies at a slightly lower temperature. The filtered blue solution deposits on cooling blue needles consisting of an ammoniacal iodide of copper and mercury containing the copper in the form of cupric iodide  $\text{CuI}^2$ . The formation of this compound is due to the mercury which is set free and remains mixed with the precipitate. When the fused mass is redissolved in boiling slightly ammoniacal water, green crystals are formed which likewise contain mercury and copper, the latter, however, in the form of cuprous iodide  $\text{CuI}^2$ ; they appear to be formed by simple addition of ammonia to the original compound, into which, indeed, they are reconverted on exposure to the air, or treatment with an acid. The blue crystals, on the other hand, which, when dried by heat, are likewise converted into a double iodide, give up iodine at the same time, even before they have parted with all their ammonia.

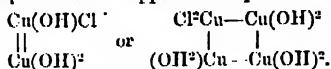
**Cuprous oxide.**—This oxide has been found in crystals (cuprite) in an ancient Russian tomb, at Dimitrow, in the Telsch district of the Kowno Dominion. At a depth of 120 c.m. below the surface, in a bed of loose yellow sand overlying compact red boulder-clay, were found a number of objects, many of them of metal. Sand being a material in which the corrosion of metallic bodies goes on more rapidly than in peat, or marsh, or water, the bronze was covered with a thick crust of malachite. On opening the grave, a lump of red ferruginous sand was found containing a necklace of wire

thread covered over with fragments of skull. In some little cavities in the crust of iron rust that covered the wire, small ruby-red crystals of cuprite ( $\infty O \infty . O . O \infty$ ) were seen. The cuprite evidently arose from the reduction by water containing ferrous carbonate, of the ammoniacal solution of copper oxide produced by the reaction of the decomposing human remains on the bronze (Growthig, *Jahrbuch f. Mineralogie*, 1871, 76).

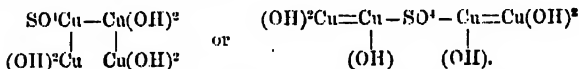
**Oxychloride.**—Crystals of atacamite from Walleroo in Australia, carefully selected and free from foreign admixtures, were found by H. Ludwig (*Deut. Chem. Ges. Ber.* vi. 553) to have the composition  $Cu^2ClH^2O^2$  or  $CuCl^2.3CuH^2O^2$ , agreeing with the older analyses by Klaproth, J. Davy and others (i. 428).

Atacamite is decomposed by heat; when it is gradually heated, water-vapour escapes and there remains a mixture of cupric oxide and cupric chloride from which the latter may be extracted by water. This decomposition, however, begins only at  $220^\circ$  and goes on but slowly at  $250^\circ$ , not being completed for several days. When the temperature rises above  $250^\circ$ , hydrochloric acid escapes with the water-vapour, and the residue, when treated with water, no longer yields the original compound. Water does not act perceptibly on atacamite, even when heated with it to  $200^\circ$  for several hours in sealed tubes.

From these results Ludwig infers that atacamite is not, as generally supposed, a molecular compound of cupric chloride with cupric hydroxide (*vid. sup.*) or of cupric oxychloride with water,  $Cu^2Cl^2O^2 + 3H^2O$ , but an atomic compound,  $Cu^2Cl^2O^2H^2$  or  $Cu^2Cl^2O^2H^2$ , containing quadrivalent copper, and represented by the structural formula



In like manner brochantite,  $Cu^2SO^4H^2$ , which is decomposed only at temperatures above  $300^\circ$ , giving off water and leaving a mixture of cupric oxide and cupric sulphate, may be regarded, not as a molecular compound,  $Cu^2SO^4.3Cu^2H^2O^2$ , containing bivalent copper, but as an atomic compound of quadrivalent copper, represented by the formula



The constitution of malachite, azurite and the so-called basic copper salts prepared artificially, may also, according to Ludwig, be more appropriately represented by atomic formulae containing quadrivalent copper, than by the usual molecular formulae.

**Sulphides.**—Native copper-glance ( $Cu^2S$ ) from Catamarca, of sp. gr. 4.7 and having distinct crystals of iron pyrites and quartz imbedded in it, gave by analysis:

Cu	S	Fe	As	Zn	SiO <sup>2</sup> (matrix)	Bi, Sb
48.82	26.71	6.64	9.16	0.74	7.52	traces = 99.59

L. Schinnerer (*Jahrbuch f. Mineralogie*, 1872, 977).

Cuprous sulphide is formed in crystals, with evolution of hydrogen, when copper turnings are digested in colourless solution of ammonium sulphide free from sulphhydrate. The crystals consist of very slender needles having a grey colour and metallic lustre: they change by oxidation on exposure to the air. On adding water or hydrochloric acid to the liquid from which they have separated, a precipitate containing copper is thrown down. Now, as the solution is colourless, the copper contained in it could not have been in the form of the red copper-ammonium sulphide described below, though perhaps a similar compound may exist containing a smaller proportion of sulphur (K. Heumann, *Deut. Chem. Ges. Ber.* vi. 748).

Cupric oxide treated with ammonium monosulphide yields a black precipitate consisting chiefly of  $Cu^2S$ , but containing a considerable quantity of  $CuS$ . The supernatant liquid treated with hydrochloric acid yields a precipitate of sulphur (Heumann).

A copper-ammonium-sulphide having the composition  $(NH^4)^2S.2CuS^2$ , is deposited in cinnabar-red needles from a hot solution of cupric sulphide in ammonium sulphide left to cool in a closed vessel (Bloxam, *Chem. Soc. J.* [2] iii. 94). It is also formed when an ammoniacal solution of the complex thiosulphate  $(Cu^2)^2Cu^2Na^2S^2O^2.3NH^4$ , described by Peltzer (v. 633), or of the yellow salt obtained from it, or a dilute ammoniacal solution of cupric sulphate, is added by drops to a solution of ammonium polysulphide till a permanent precipitate is formed, and the solution is filtered into a flask which must be quite filled with it and closed air-tight. After a day or two the double sulphide separates in small garnet-red concentrically grouped needles, or as an amorphous powder if the liquid is shaken.

This sulphur salt dissolves with yellow colour in water and ammonia, and

in alkaline carbonates. According to Bloxam, it is not decomposed by cold hydrochloric or nitric acid; according to Peltzer, on the other hand, it is decomposed by dilute acids, with evolution of hydrogen sulphide and separation of red-brown or black-brown copper sulphide, but without separation of sulphur. When heated with potash it appears to be at first converted, with evolution of ammonia, into the corresponding potassium-compound, but afterwards black copper sulphide is precipitated. Heated in a glass tube it gives off sulphur and ammonium sulphide (Peltzer).

**CORALLIN.** The names *Red Corallin* and *Peonin* (iv. 324), have been given to the red colouring matter which Kolbe a. Schmitt obtained by treating phenol with sulphuric and oxalic acids. This body has been further examined by H. Fresenius (*J. pr. Chem.* [2] v. 184; *Chem. Soc. J.* [2] x. 705), who purifies it by combining it with magnesia, and afterwards decomposing the compound with sal-ammoniac. Crystallised from alcohol it forms filamentous, interlacing, scarlet, lustrous crystals; crystallised from glacial acetic acid, it forms magnificent rhombic crystals which are combinations of the prism  $\infty P$  with a second prism not determined, the brachy-pinacoid,  $\infty P_{\infty}$ , and sometimes the brachydome  $\bar{P}_{\infty}$ . Ratio of axes  $a : b : c = 0.541 : 1 : 0.354$ ; angle  $\infty P : \infty P = 123^{\circ} 3'$ ;  $\infty P : \infty P_{\infty} = 118^{\circ} 25'$ ;  $\bar{P}_{\infty} : \bar{P}_{\infty} = 141^{\circ} 5'$ ;  $\bar{P}_{\infty} : \infty P_{\infty} = 109^{\circ} 29'$ . Cleavage distinct parallel to  $OP$ .

The crystals are red by transmitted, dark green by reflected light, moderately soluble in phenol, slightly in boiling chloroform and boiling benzene, insoluble in carbon bisulphide; become strongly electric when rubbed. They melt at  $156^{\circ}$ . Kolbe a. Schmitt found the melting point to be  $80^{\circ}$ , probably because their product still retained considerable quantities of phenol.

Corallin gives by analysis (mean) 69.07 p.c. carbon, and 5.38 hydrogen, agreeing with the formula  $C^{10}H^{10}O^{11}$  which requires 69.18 carbon and 5.47 hydrogen. Regarding again as  $C^{10}H^{10}O^{11}$  (p. 118), the relation between these two compounds may be expressed by the equation  $2C^{10}H^{10}O^{11} + 5H^{10}O = C^{10}H^{10}O^{11}$ .

The mode of formation of corallin, however, suggests a simpler formula: for the gas which escapes during its preparation by oxalic acid is chiefly carbon dioxide: hence it is inferred that the substance which is most active in its formation is carbon monoxide derived from the oxalic acid: and this conclusion is corroborated by the fact that formic acid may be used in preparing corallin, in place of oxalic acid. Hence Kolbe, in a note to Fresenius' paper, suggests that corallin is formylated phenol  $C^8H^8O^2 = C^8H^4(COH)OH$ , its formation being represented by the equation



The formula  $C^8H^8O^2$  requires 68.85 p.c. carbon and 4.90 hydrogen.

Corallin is likewise obtained when phenetol or anisol is substituted for phenol in its preparation; also when meta- or para-phenylsulphonic acid is acted upon by oxalic acid.

Caro a. Wanklyn's rosolic acid, obtained by the action of nitrous acid on rosaniline is different from corallin; its composition being, according to analyses by Fresenius,  $C^{12}H^{12}O^{10}$  (Caro a. Wanklyn gave the formula  $C^{12}H^{12}O^4$ ), it melts at about  $158^{\circ}$ , and its alcoholic solution is not decolorised, like that of corallin, by concentrated solution of acid sodium sulphite. Fresenius proposes to call this body *pseudocorallin*.

**Printing with Corallin.**—Corallin is much used for dyeing on wool, and may also be employed for printing on wool, provided some means be adopted for neutralising the acids with which it is sure to come in contact in the course of treatment to which it is subjected. The effect of the acids, which is to cause the red colour to fade into yellow, may be prevented by the use of calcined magnesia, the corallin being dissolved in water or in alcohol. The resulting colour is a rich Turkey-red, which maintains its intensity and brilliancy for years. This red is about 30 p.c. cheaper than cochineal red, and has this advantage over the latter, that it is not turned blue by washing in water containing calcium carbonate, the only disadvantage being that of its fading in contact with strongly acid colours, if the acid be more than sufficient to neutralise the magnesia. The following mixture is recommended for printing:—80 grams corallin,  $\frac{1}{2}$  litre glycerin,  $\frac{1}{2}$  litre water, 140 grams magnesia, well stirred up with  $\frac{1}{2}$  litre of water. The whole is thickened with  $\frac{1}{2}$  litre of gum-water (500 grams to the litre), and printed, steamed, and washed in the usual way.

Corallin may also be printed on cotton, the colour being thickened with starch and egg-albumin in addition to magnesia. This mixture must be used fresh, as in time an insoluble compound is formed between the magnesia and the albumin (*Diag. polyt. J. civ. 338*).

**CORIARIA.** The poisonous principle of the Tutu plant (*Coriaria ruscifolia*) of New Zealand does not appear to be of the nature of an alkaloid. The ground seeds repeatedly treated with alcohol yield a greenish-red substance, which, when





**CREATINE**,  $C_4H_7N^3O_2$ . A compound isomeric with creatine, called isocreatine or alacreatine, is formed by direct combination of alanine with cyanamide:  $C_2H_5NO_2 + CH_3N^2 = C_4H_7N^3O_2$ . When a concentrated aqueous solution of the two substances mixed with a little ammonia is left to stand for some time, dicyanamide crystallises out first, and then alacreatine, the yield of which may be increased by employing an excess of alanine, but never reaches the theoretical limit.

Alacreatine forms anhydrous prismatic crystals resembling creatine. It is almost insoluble in cold alcohol, and very sparingly soluble in hot alcohol, but dissolves freely in water, namely, in 12 parts at  $15^\circ$ , whereas creatine, according to Liebig, requires 71 parts at  $18^\circ$ . When heated to  $170^\circ$ – $180^\circ$ , or treated with dilute sulphuric acid, it loses water and is converted into alacreatinine,  $C_4H_7N^3O$ , which dissolves in water and in alcohol more freely than alacreatine, crystallises from water in long needles resembling urea, and from alcohol in small rhombohedral anhydrous crystals (E. Baumann, *Ann. Ch. Pharm.* clix. 77).

**CREATININE**.  $C_4H_7NO$ .—*Preparation from Urine*.—A few litres of human urine are evaporated to about one-third of the original volume, and the liquid, after being decanted from the salts which crystallise out, is precipitated with lead acetate. The filtrate is freed from lead by sodium carbonate or sulphuretted hydrogen, neutralised either with acetic acid or with sodium carbonate, and precipitated with mercuric chloride. The precipitate, a combination of creatinine with the mercuric salt, is decomposed under water with sulphuretted hydrogen, and the liquid, after treatment with animal charcoal, is evaporated. On recrystallising the crystalline residue once or twice from alcohol, pure creatinine hydrochloride is obtained in white crusts or hard shining prisms. The same results were obtained with horses' urine (Maly, *Ann. Ch. Pharm.* clix. 279).

Alacreatinine, obtained, as above described, by dehydration of alacreatine, dissolves in alcohol and water more freely than the latter, crystallises from water in long needles resembling urea, and from alcohol in small anhydrous rhombohedral crystals, which, on exposure to the air, absorb water and change into needles. Alacreatinine is a base resembling creatinine, and forming double salts with zinc chloride and other chlorides. It also reduces mercuric oxide, yielding, together with other products, an alkaline base, but no oxalic acid (Baumann, *loc. cit.*)

**CRENIC ACID**. According to Bontigny (*Compt. rend.* lviii. 247), the medicinal waters of Forges-les-Baux contain ferrous salts of crenic and apocrenic acids. On exposure to air the waters deposit an insoluble ferric compound, from which crenic acid can be extracted by boiling with caustic potash and precipitating the solution with hydrochloric acid. The purified crenic acid is capable of dissolving ferrous carbonate. The source of the waters is a peaty stratum, overlying a vein of iron pyrites.

**CRESOL**.  $C^6H^3O = C^6H^4 \begin{Bmatrix} CH^3 \\ OH \end{Bmatrix}$ . H. L. Buff (*Deut. Chem. Ges. Ber.* iv. 378) has obtained a solid and a liquid cresol by subjecting coal-tar creasote to fractional solution in soda-ley, and fractional precipitation with hydrochloric acid; treating the fraction boiling at  $204^\circ$ – $205^\circ$  with benzoyl chloride, whereby a solid and a liquid cresyl benzoate were produced; and decomposing these ethers with alcoholic potash. The solid body was obtained in large, white, hard crystals, which melted at  $70^\circ$ – $70.5^\circ$ , and solidified at  $52.6^\circ$ . Its properties agree with those of paracresyl benzoate, which melts at  $70^\circ$ . The cresol obtained from it is a colourless body, having a sharp urinous smell. It solidifies in a mixture of ammonium sulphocyanate and water, melts at  $34^\circ$ , and boils at  $205^\circ$ . Its properties are those of paracresol (*1st Suppl.* 608).

The liquid ether boils above  $360^\circ$ , and does not solidify in a mixture of ammonium sulphocyanate and water. The cresol separated from it by alcoholic potash cannot be made to solidify; after fusion with potash, it gives, with ferric chloride, the reaction of salicylic acid.

Chlorocresol,  $C^6H^3Cl \begin{Bmatrix} CH^3 \\ OH \end{Bmatrix}$ , may be prepared by heating cresol-vapour with chlorine, removing the resulting hydrochloric acid by a stream of carbonic anhydride, subjecting the product to fractional distillation, and separating the portion which distils between  $235^\circ$  and  $245^\circ$ . This liquid, when cooled by a freezing mixture, deposits crystals of chloro-cresol, easily soluble in alcohol, ether, benzene, and petroleum oil, melting at  $56^\circ$ , boiling at about  $240^\circ$ . This compound does not yield any definite products with ammonia, aniline, potassium cyanide or silver cyanide; neither can orcin be produced from it by heating with alcoholic potash or fusion with potassium hydrate. Hence it may be inferred that the chlorine-atom is contained, not in the lateral chain  $CH^3$ —as might perhaps have been expected from the formation of the compound at a

high temperature—but in the benzene nucleus, as indicated by the formula above given (R. Biedermann, *Deut. Chem. Ber.* vi. 325).

Cresol-sulphonic acid,  $C^6H^5SO^4 = C^6H^5 \begin{Bmatrix} CH^3 \\ SO^3H \\ OH \end{Bmatrix}$ , was prepared by heating

sulphuric acid and the above-mentioned cresol to 60°. The barium salt and calcium salt are very soluble, crystallise badly, and have a tendency to form basic salts. The potassium salt forms star-shaped groups containing two molecules of water. The salts of this acid appear to correspond with those of the  $\gamma$ -cresol-sulphuric acid of Engelhardt and Latschinoff (*1st Suppl.* 507). On fusing the potassium salt with potash and treating the product in the usual way, pyrocatechin was obtained, but no orcin (Biedermann).

With the view of obtaining orcin, cresol was treated with an alkaline solution of iodic acid and iodine, according to the method of Körner, whereby an iodised cresol was obtained in the form of an oil which decomposed below its boiling point, and this oil heated to 250°–300° with alcoholic potash, was decomposed, yielding a brown amorphous mass. This substance was several times dissolved in an alkali and precipitated by an acid, and was afterwards purified by various solvents. It becomes red on treatment with ammonia, dissolves in alkalis with a dark red colour, softens at 50°, melts at 100°, and is free from iodine. By analysis it gave numbers agreeing with the formula  $C^6H^5IO^3$  or  $\begin{Bmatrix} CH^3 \\ HO \end{Bmatrix} C^6H^5-O-C^6H^5 \begin{Bmatrix} CH^3 \\ OH \end{Bmatrix}$  (Biedermann).

**CRESOTIC ACID**,  $C^6H^5O^3 = C^6H^5 \begin{Bmatrix} CH^3 \\ OH \\ CO^2H \end{Bmatrix}$ . Biedermann a. Pike (*Deut. Chem.*

*Ges. Ber.* vi. 323) have prepared this acid from coal-tar cresol obtained from Calvert's manufactory. This liquid did not yield to fractional distillation any product of constant boiling point, but the portion boiling at 203° was regarded as pure cresol.

Cresotic acid was prepared, according to Kolbe's method (*1st Suppl.* 508), by dissolving sodium in the cresol, and passing carbonic anhydride into the solution; the sodium cresotate was then precipitated from the liquid by a concentrated solution of ammonium carbonate, and pure cresotic acid was separated from the aqueous solution of the precipitate by hydrochloric acid. It was found, however, that only a small portion of the cresol is converted by this treatment into cresotic acid, probably because one of the modifications of cresol in the mixture is more easily acted on than the other two.

Cresotic acid thus prepared melts at 174°. According to Kolbe, the melting point is 153°. Engelhardt a. Latschinoff, on the other hand, found that the cresotic acid which they prepared from  $\gamma$ -cresol or meta-cresol by the action of phosphoric anhydride on thymol (*1st Suppl.* 507), melted at 168°–173°, whereas the melting points of their  $\alpha$  and  $\beta$  cresotic acids (prepared by fusing  $\alpha$ - and  $\beta$ -toluenesulphonate of potassium with potash) were much lower, viz., 114° and 147°–150° respectively. It would appear, then, that the cresotic acid prepared as above is  $\gamma$ -cresotic or meta-cresotic acid.

This cresotic acid crystallises from water in beautiful shining needles resembling salicylic acid, and strikes a deep violet colour with ferric chloride. The calcium salt and barium salt are very soluble in water, crystallise badly, and retain no water of crystallisation. The silver salt forms a white powder soluble in hot water, and yields methyl cresotate when it is heated with methyl iodide. This ether boils at 236°–237°, and smells like gaultheria oil. Alkalis act on it, forming an alkaline methyl-cresotate, which by further treatment with alkali splits up into methylic alcohol and cresotic acid. Ammonia converts it into methyl alcohol and cresotamide, a solid slightly soluble mass, which has not yet been investigated.

An attempt to prepare the aldehyde of cresotic acid by the distillation of calcium cresotate and calcium formate was unsuccessful, cresol and other products not yet investigated being formed. Nothing giving a crystalline product with sodium bisulphite was obtained.

**CRONSTEDTITE.** This mineral, found only at Příbram in Bohemia, and in Cornwall, was first analysed by von Kobell, who assigned to it the formula  $3(FeO \cdot SiO_2) \cdot 4(Fe_2O_3 \cdot 3H_2O)$ , or  $3Fe^{+2}SiO_3 \cdot 4(Fe^{+3})^{+}H_2O^6$  (ii. 112). This formula has recently been confirmed by Maskelyne a. Flight (*Chem. Soc. J.* [2] ix. 9), who found in a well selected Cornish specimen, 41.27 p.c. ferrous oxide, the formula requiring 41.54. Many specimens, however, exhibit a smaller percentage of ferrous oxide, and an excess of ferric oxide, probably from association with a ferric silicate, like hisingerite, with which, indeed, cronstedtite has been shown to be associated.

The crystals of cronstedtite belong to the hexagonal system and are hemimorphous. The specimens formerly examined from Příbram and from Wheal Maudlin in Cornwall

did not yield measurable crystals; but amongst those from other Cornish localities examined by Maskelyne and Flight, were a few on which the diverging groups of the crystals of cronstedtite presented here and there a crystal, or more generally a small group of crystals, with more definite features. In some cases the crystals were mutually interpenetrating, the brilliant cleavage-planes of the different crystals projecting through one another, and presenting re-entering angles which indicated the probability of their being twinned. In most cases, again, a careful scrutiny of the bright summit plane showed that it was tessellated, and that the crystal was in fact composite, the different individuals comprising it being generally in parallel juxtaposition (fig. 9), but sometimes (fig. 10) twinned round the normal to that plane (the morphological axis of the crystal); but never so as to mask the truly hemimorphous character of the crystal. The symmetry round the axis of each crystal is trigonal, the form of the crystal being that resulting from the combination of two rhombohedrons, of which only the planes on one side of the unique plane of symmetry (that parallel to the summit plane) are extant. The crystal thus presents the aspect of a combination of two trigonal pyramids, of which one is more acute than the other (fig. 11). For angular measurements see the original paper.

FIG. 9.

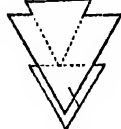
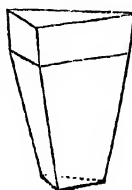


FIG. 10.



FIG. 11.



#### CROTON OIL, ACIDS OBTAINED FROM.

It has hitherto been admitted, on the authority of Schlippe, that croton oil yields by saponification crotonic acid  $C_4H_7O_2$  and angelic acid  $C_4H_5O_2$  (ii. 112). But from recent experiments by Geuther and Fröhlich (*Zeitschr. f. Chem.* [2] vi. 26, 549), it appears that this oil does not yield any liquid acid having the composition  $C_4H_7O_2$ , and that the solid acid,  $C_4H_5O_2$ , which it yields, is not angelic acid.

Croton oil (2 kilo.) is saponified with strong soda-ley; the brown soap removed; the black under-liquor supersaturated with sulphuric acid and distilled; the distillate (on which oil-drops float) is neutralised with sodium carbonate, then evaporated to a small bulk and supersaturated with sulphuric acid; the acids which separate in oily form are removed from the watery liquid; the latter is several times exhausted with ether free from alcohol; the ether added to the oily acids; the ethereal liquid dehydrated with calcium chloride; and the ether distilled off. By this process, a brown oil is obtained as residue (44 grams) which by repeated fractional distillation may be separated into four portions, the first boiling at  $115^\circ$ – $160^\circ$ , the second at  $160^\circ$ – $190^\circ$ , the third at  $190^\circ$ – $205^\circ$ , and the fourth at  $205^\circ$ – $270^\circ$ .

The first fraction contains butyric and acetic acids (no propionic acid was observed); the second, butyric and valeric acids. The third contains a crystallised acid, constituting nearly the whole, which has the constitution of angelic acid, but is not identical therewith. When freed from adhering oily acid by repeated crystallisation from water, this acid forms transparent, colourless, rhombic plates and prisms, which at  $61^\circ$  begin to melt at the edges, and at  $64^\circ$  melt completely to a limpid oil, gradually solidifying again between  $60^\circ$  and  $58^\circ$ . It boils without decomposition at  $201.1^\circ$  (corr.), tastes very sour, and when pure has a pleasant aromatic odour. Geuther and Fröhlich designate this acid provisionally as tiglic acid, and point out that it is, perhaps, identical with Frankland and Duppa's methyl-crotonic acid (1st Suppl. 828). Its ethylic ether  $C_4H_7O_2.C_2H_5$  boils at  $160^\circ$  (corr.), has a specific gravity of 0.926, is colourless, transparent, and insoluble in water, and has a peculiar aromatic odour, not at all like the disagreeable odour ascribed by Frankland and Duppa to methyl-crotonic ether.

Barium tiglate,  $(C_4H_5O_2)_2Ba + 10H_2O$ , separates from its aqueous solution on evaporation, as a dense crystalline mass made up of small needles; it is very soluble in water, but by no means difficult to crystallise, as the methyl-crotonate is said to be. It gives up its water of crystallisation over oil of vitriol. Silver tiglate  $C_4H_5O_2AgO_2$  is a white crystalline powder, nearly insoluble in water, and but little altered by light.

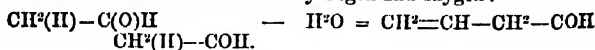
The fourth fraction ( $205^\circ$ – $270^\circ$ ) of the original mixture of acids appears to contain caproic, or cennanthylic, or pyroterebic acid, together with higher members of the

acrylic series or of the next lower isologous series  $C^aH^{a-1}O^2$ : the quantity of this fraction is, however, very small.

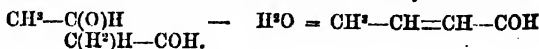
**CROTONIC ACID.**  $CH^2H^2O^2$  (Kekulé, *Deut. Chem. Ges. Ber.* iii. 604; *Zeitschr. f. Chem.* [2] vi. 705). Solid crotonic acid (hitherto distinguished as  $\alpha$ -crotonic acid) is produced by the action of oxygen or atmospheric air on crotonic aldehyde (formed by condensation of acetic aldehyde),—also as a silver salt by oxidising crotonic aldehyde with silver oxide. The acid thus produced melts at  $71^\circ$ – $72^\circ$ . In a small distilling flask it boils at  $180^\circ$ – $181^\circ$ ; when distilled according to Kopp's directions, at  $182^\circ$  (corr.  $181^\circ$ ); with the mercury-column entirely in the vapour, at  $189^\circ$ . In vessels exposed to the sun, it sublimes in large rhombic plates. It dissolves in 12.47 parts of water at  $19^\circ$  and is obtained by evaporation of this solution in well-defined monoclinic crystals exhibiting the combination  $\infty P$ ,  $\infty P \infty$ ,  $OP$ ,  $+ P \infty$ . Angle  $\infty P$ :  $OP = 112^\circ 50'$ ;  $\infty P$ :  $\infty P = 107^\circ 30'$  (laterally);  $OP$ :  $+ P \infty = 125^\circ 30'$ . Axes  $a$ :  $b$ :  $c = 1$ :  $1.8065$ :  $1.5125$ . Angle  $bc = 131^\circ$ . Cleavage parallel to  $OP$  and  $\infty P \infty$  (vom Rath). When fused with potash, it yields nothing but acetic acid.

The same characters are exhibited by crotonic acid prepared from the allyl cyanide obtained from mustard oil (1st *Suppl.* 510). According to Will a. Körner, this acid melts at  $72^\circ$ ; according to Bulk, it melts at  $72^\circ$ , boils at  $183.8^\circ$  (corr.  $187^\circ$ ), and dissolves in 12.07 parts water at  $15^\circ$ . With regard to the crystalline form, Bulk gives measurements by Knop, from which, it appears that the crystals of the acid are monoclinic. Knop's measurements (*Ann. Ch. Pharm.* cxxxix. 62) are indeed affected with certain obvious errors, but four out of the six angles measured by him agree nearly with those determined by von Rath. The identity of the crotonic acid from allyl cyanide prepared from mustard oil with that obtained by oxidation of crotonic aldehyde, is therefore established; and the same may be said of the acid which Wislicenus obtained by the distillation of  $\beta$ -oxybutyric acid, which melts at  $71^\circ$ – $72^\circ$  and boils at  $181^\circ$ – $182^\circ$  (corr.) The crotonic acid obtained from allyl cyanide synthetically prepared (by the action of potassium or silver cyanide on allyl iodide) likewise exhibits the same physical properties, but according to Claus (*Deut. Chem. Ges. Ber.* iii. 93), when fused with potash, it yields, not acetic, but propionic and carbonic acids. Kekulé, however, finds that this statement is erroneous. He prepared crotonic acid in the manner described by Claus, viz., by converting allyl iodide into the cyanide, and distilling the latter with potash, and purified the portion distilling between  $180^\circ$  and  $195^\circ$  by converting it into the sparingly soluble silver salt and separating the acid therefrom. The crotonic acid thus obtained melted at  $72^\circ$ , boiled at  $182^\circ$ , and gave by fusion with potash, nothing but acetic acid.

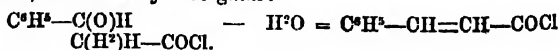
**Constitution of Solid Crotonic acid.**—The identity of the crotonic acid from crotonic aldehyde and from allyl cyanide being thus established, it would seem to follow that this crotonic acid must have the formula  $CH^2=CH-CH^2-COOH$ , inasmuch as the constitution of allyl alcohol is constantly represented by the formula  $CH^2=CH-CH^2OH$ , and, therefore, that of allyl cyanide by  $CH^2=CH-CH^2-CN$ ; and, in fact, Kekulé formerly represented crotonic acid by the formula just mentioned, assigning, also, a similar constitution to crotonic aldehyde, and supposing it to be formed from acetic aldehyde in the manner shown by the following equation, in which the bracketted symbols indicate the eliminated atoms of hydrogen and oxygen:



(See 1st *Suppl.* p. 513). Now, however, he considers it more probable that the two hydrogen-atoms are taken, not one from each of the methyl groups present, as above, but both from the same methyl group, giving for the resulting crotonic aldehyde a formula in which the two middle carbon-atoms are doubly linked, thus:



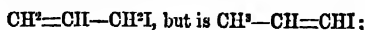
That such is the true representation of the change may be inferred with great probability from the analogous synthesis of cinnamyl chloride from benzoic aldehyde and acetyl chloride, discovered by Bortagnini:



In this case it can scarcely be supposed that the carbon-atom already attached to the aromatic nucleus by one unit of affinity could become more intimately united with it, so as to form the group  $C^aH^2=CH-$ .

Admitting, then, for crotonic aldehyde the formula  $CH^2-CH=CH-COH$ , it follows that the crotonic acid formed from it, and therefore also, the acid formed from

allyl alcohol, must have the constitution  $\text{CH}^2=\text{CH}=\text{CH}-\text{COOH}$ . In the latter case it must be supposed that, at some stage in the passage from the alcohol to the acid, a change occurs in the arrangement of the hydrogen-atoms, either that the iodide prepared from the alcohol has no longer the formula—



or that the cyanide is not—



or that the cyanide constituted according to the first formula yields an acid corresponding to the second cyanide.

The formula thus assigned to crotonic acid is confirmed by the fact that when fused with alkalis it is resolved into two molecules of acetic acid. For all the acids of the acrylic series when thus treated, split up at the point where the carbon-atoms are doubly united (1st *Suppl.* 42), so that when the molecule  $\text{CH}^2=\text{CH}=\text{CH}-\text{CO}^2\text{H}$  is acted upon by  $2\text{H}^2\text{O}$  (or  $2\text{KHO}$ ), the group  $\text{CH}^2-\text{CH}$  takes up 2 atoms of oxygen, and the right-hand group  $\text{CH}-\text{CO}^2\text{H}$  takes up 2 atoms of hydrogen, forming 2 mols. acetic acid  $\text{CH}^3-\text{CO}^2\text{H}$ , while the remaining 2 atoms of hydrogen are eliminated. An acid having the constitution  $\text{CH}^2=\text{CH}-\text{CH}^2-\text{CO}^2\text{H}$  would split up, under similar circumstances, into formic and propionic acids.

The formula  $\text{CH}^2=\text{CH}=\text{CH}-\text{COOH}$  was formerly assigned to the liquid crotonic acid said to be obtained, 1. by saponification of croton oil (Schlieper); 2. by the action of chloroethylidene and metallic silver on chloroacetic acid (Stacewitz); 3. by the action of nascent hydrogen on the modification of chlorocrotonic acid which melts at  $59.5$  (Geuther; see 1st *Suppl.* 509). With regard to the first of these products, it appears, from the experiments of Geuther & Fröhlich, that the saponification of croton oil does not yield any acid having the composition  $\text{C}^4\text{H}^6\text{O}^2$  (p. 395). With regard to the second, it has been shown by Kekulé & Zincke (*Ann. Chem. Pharm.* cxlii. 125) that the supposed isomeride of chloroethylene or vinyl chloride, called *chloracetylene* or *chloroethylidene*, said by Harnitzky to be formed by the action of phosgene on aldehyde, has no existence; hence it is probable that the liquid product obtained in the second of the above-mentioned reactions was nothing but crotonic aldehyde (formed by the action of hydrochloric acid on the acetic aldehyde) mixed with hydrochloric acid.

The liquid crotonic acid obtained by the third reaction, called *quartenylic* acid by Geuther, is said by him to yield nothing but acetic acid when fused with potash; but this, according to Kekulé, is the reaction exhibited by solid crotonic acid: hence Kekulé considers the existence of this liquid crotonic acid as somewhat doubtful, and suggests that it should have been confirmed by converting the acid in question into a silver salt and separating it therefrom. The chlorocrotonic acid of higher melting point is converted by nascent hydrogen into solid crotonic acid.

On the whole, then, Kekulé considers that only two modifications of the acid  $\text{C}^4\text{H}^6\text{O}^2$  have as yet been satisfactorily made out, viz:

Crotonic acid (solid).  $\text{CH}^2=\text{CH}=\text{CH}-\text{COOH}$ .

Methacrylic acid.

$$\begin{array}{c} \text{H}^2\text{C} \\ \diagdown \\ \text{C}-\text{COOH} \\ \diagup \\ \text{H}^2\text{C} \end{array}$$

The third modification,  $\text{CH}^2=\text{CH}-\text{CH}^2-\text{COOH}$ , remains to be discovered.

On the constitution of crotonic acid see also Paternò (*Zeitschr. f. Chem.* [2] vi. 88); Lwow (*ibid.* 245).

**Chlorocrotonic acids.**—Trichlorocrotonic acid,  $\text{C}^4\text{H}^2\text{Cl}^3\text{O}^2$ , is produced by oxidation of crotonic chloral with fuming nitric acid. The action is very violent and must be moderated by cooling; with impure crotonic chloral it takes place immediately, but with the pure substance, after some time only. The trichlorocrotonic acid obtained from somewhat impure crotonic chloral often remains liquid for several days, and crystallises only in contact with crystals of the pure acid.

Trichlorocrotonic acid crystallises in colourless radiate needles, melting at  $44^\circ$  and boiling at  $236^\circ-238^\circ$ ; it is very caustic, and destroys the skin. It takes up 33 p.c. of water, and, on the other hand, 25 parts of water dissolve one part of the acid. By acting upon it with zinc and hydrochloric acid the chlorine is replaced by hydrogen. All the products thus obtained crystallise well; best of all, *monochlorocrotonic acid*, which melts at  $95^\circ$  (Judson, *Zeitschr. f. Chem.* [2], vii. 40).

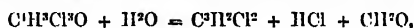
*Potassium trichlorocrotonate*,  $\text{C}^4\text{H}^2\text{KCl}^3\text{O}^2$ , is obtained by adding potassium carbonate slowly and in small quantities to the moderately concentrated acid; it crystallises in prisms and is very hygroscopic. *Ammonium trichlorocrotonate*,  $\text{C}^4\text{H}^2(\text{NH}^4)\text{Cl}^3\text{O}^2$ ,

crystallises from alcohol in colourless scales. *Lead trichlorocrotonate*,  $(C^4H^3Cl^3O)_2Pb + 2H^2O$ , is prepared by shaking an ethereal solution of the acid with lead carbonate. On evaporating the solution, the salt crystallises in needles arranged in tuft-like groups; it is insoluble in cold water and sparingly soluble in boiling water. *Silver trichlorocrotonate*,  $C^4H^3AgCl^3O^2$ , is obtained by mixing moist silver oxide with a dilute solution of the acid, and adding silver nitrate and ammonia to the filtrate until it shows a slight alkaline reaction; the salt is thus obtained as a crystalline precipitate, which may be dried in vacuo. The *ethylic ether*,  $C^4H^3C^2H^5O^2.C^2H^5$ , is formed by heating equal numbers of molecules of the acid and ethyl alcohol in sealed tubes for some hours to  $100^\circ$ . It is a colourless, heavy liquid, which boils at  $212^\circ$  and has an aromatic odour (Judson).

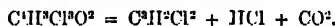
*Trichlorocrotonyl chloride*,  $C^4H^3Cl^3OCl$ , a heavy liquid, boiling at  $162^\circ$ – $166^\circ$ , is prepared by heating the acid with phosphoric chloride to  $120^\circ$ . Water acts on it slowly, but by alcohol it is instantaneously decomposed, ethylic trichlorocrotonate being formed (Judson).

*Trichlorocrotonamide*,  $C^4H^3Cl^3ONH^2$ , is easily formed by pouring aqueous ammonia over the chloride. It is sparingly soluble in cold, more readily in boiling water, and crystallises from alcohol and ether in silvery scales, which melt at  $96^\circ$  (Judson).

When silver trichlorocrotonate is heated with water in a flask connected with a reversed condenser, a brisk evolution of carbonic acid takes place, and silver chloride and *dichlorallylene*,  $C^2H^2Cl^2$ , are formed. The latter is a heavy oil which has a penetrating odour: it boils at  $78^\circ$  and combines readily with bromine. The same compound is obtained by acting on crotonic chloral with caustic baryta—



or by heating trichlorocrotonic acid with dilute alkalis—



If the aqueous solution of the acid is treated with an excess of silver oxide or alkali, the yield of dichlorallylene is very small, as the action goes further (Judson).

*Monochlorocrotonic acid*,  $C^4H^3ClO^2$ .—The zinc-salt of this acid is formed by the action of zinc and hydrochloric acid on trichlorocrotonic acid (p. 397); or by slowly dropping fused trichlorocrotonic acid into a mixture of water and zinc-dust; the mixture then becomes warm, and no gas is evolved; but if too much of the trichlorinated acid is added at once, a gas is evolved which burns with a green flame and probably contains carbon and chlorine. By treating the solution of the zinc salt with hydrochloric or sulphuric acid, crude monochlorocrotonic acid is precipitated; it may be purified by recrystallisation from hot water, in which it easily dissolves. It is easily soluble also in alcohol and ether, melts at  $96^\circ$ , boils at  $212^\circ$ , and sublimes partially even at the heat of the water-bath, forming pearly scales and needles. It is not dechlorinated by treating it in aqueous solution with zinc-dust or silver oxide, or by heating it with ammonia to  $120^\circ$ ; but by treating a concentrated solution of sodium monochlorocrotonate with sodium-amalgam, and decomposing the resulting sodium salt with sulphuric or hydrochloric acid, crotonic acid is obtained, identical in every respect with that which is formed from allyl cyanide or from crotonic aldehyde. On adding a molecule of bromine to a solution containing a molecule of monochlorocrotonic acid, the two unite, forming monochloro-dibromo-butyric acid  $C^4H^3ClBr^2O^2$ , which separates as a colourless oil, soon becoming crystalline. *Potassium monochlorocrotonate*,  $C^4H^3ClO^2K$ , is very readily soluble in water, and crystallises therefrom in needles, and from its alcoholic solution in plates. The *sodium salt*,  $C^4H^3ClO^2Na$ , is uncrystallisable. The *ammonium salt*,  $C^4H^3ClO^2(NH^4)$  forms large plates, or six-sided tables, which sublime readily at  $100^\circ$ . The *silver salt*,  $C^4H^3ClO^2Ag$ , is somewhat difficultly soluble in water, from which it crystallises in long white needles. The *lead salt*,  $(C^4H^3ClO^2)^2Pb + H^2O$ , forms glistening plates and needles. The *basic cupric salt*,  $(C^4H^3ClO^2)^2Cu.Cu(OH)^2$ , is precipitated as an amorphous bright blue powder, on adding cupric sulphate to a solution of an alkaline monochlorocrotonate; the *neutral salt*, which forms fine blue prisms, is obtained by evaporating over sulphuric acid a solution of cupric carbonate in the acid; the *calcium salt*,  $(C^4H^3ClO^2)^2Ca$ , crystallises in thick prisms, and the *barium salt*,  $(C^4H^3ClO^2)^2Ba$ , in thin plates which are more readily soluble than the calcium salt. *Ethyl monochlorocrotonate*,  $C^4H^3ClO^2.C^2H^5$ , formed on saturating an alcoholic solution of the acid with hydrochloric acid, is a colourless liquid, having a pleasant fruity odour, and boiling at  $176^\circ$  (Sarnow, *Deut. Chem. Ges. Ber.* iv. 731; v. 467).

*Chlorinated acids*,  $C^4H^3ClO^2$ , produced by the action of Phosphorus Pentachloride on Ethyl-diacetic acid (Geuthner, *Jenaische Zeitschrift*, vi. part 4; *Chem. Soc. J.* [2] ix. 812).—When phosphorus pentachloride (33 parts) is gradually

added to ethyldiacetic acid (10 parts), it dissolves without any great evolution of heat, forming a reddish-brown liquid; at the same time large quantities of hydrochloric acid and ethyl chloride are evolved, but no acetyl chloride is formed. The product, which consists of phosphorus oxychloride and the chlorides of several acids, cannot be successfully separated by fractional distillation, and must therefore be added gradually to water maintained at a low temperature, in which it readily dissolves. On distilling the aqueous solution, an oil first passes over with the vapour of water, which does not solidify; this is succeeded by a milky liquid which deposits crystals on cooling; and ultimately the distillate comes over clear. The first portion of the distillate contains a readily volatile oil, which does not solidify; the milky intermediate portion consists of a volatile acid which solidifies on cooling; the residue in the retort is a very difficultly volatile acid. These three may be more completely separated from one another by repeated fractional distillation with water. The small portion of the volatile acid which accompanies the neutral oil may be removed by agitating it with an excess of a solution of sodium carbonate, and distilling, the crystalline volatile acid being recovered from the sodium salt by distillation with dilute sulphuric acid. To obtain the slightly volatile acid from the residue in the retort in the first distillation, it is neutralised with sodium carbonate, and, after separation of the resinous impurities, concentrated by evaporation. Much of the sodium phosphate may thus be separated by crystallisation; and on evaporating the mother-liquors to dryness, and extracting with alcohol, the sodium salt of the new acid is dissolved, leaving the sodium phosphate and sodium chloride. After the alcohol has been removed by distillation, excess of sulphuric acid is added to the solution, and the whole boiled for some time to remove the last traces of the more volatile acid. On agitating with ether, drying the ethereal solution of the acid with calcium chloride, and evaporating, an oil is left behind, which solidifies over concentrated sulphuric acid to a crystalline mass. To purify this acid it is dissolved in water, decolorised by animal charcoal, and recrystallised.

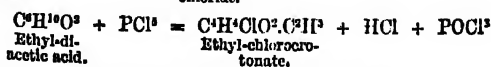
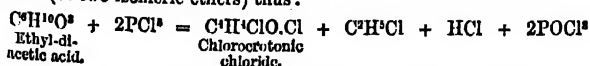
Both the acids thus obtained have the composition  $C^4H^5ClO^2$ . The less volatile acid melts at  $94^\circ$ , boils at  $206^\circ-211^\circ$ , and is identical in every respect with the monochlorocrotonic acid above described. Geuther, however, designates it as chlorotetraacrylic acid. By reduction with sodium amalgam, it is converted into solid crotonic acid (Geuther's tetraacrylic acid) melting at  $71.5^\circ$  and boiling at  $187.4^\circ$  (corr.) By the action of potassium hydrate it is converted, according to Geuther, into an acid  $C^4H^5O^2$ , which he calls tetrolic acid, melting at  $76.5^\circ$  and boiling at  $203^\circ$ . This, however, is very doubtful, as, according to all other authorities, crotonic acid fused with potash yields nothing but acetic acid.

The more volatile chlorinated acid designated by Geuther as chloro-quartenylic acid may be boiled with excess of potash without undergoing decomposition. A saturated solution of its sodium salt treated with sodium amalgam yields the sodium salt of 'quartenylic acid,' or liquid crotonic acid,  $C^4H^5O^2$ , from which that acid may be obtained as a colourless oil which boils after rectification at  $171.9^\circ$  (corr.), has a density of 0.1018 at  $25^\circ$  and does not solidify at  $-15^\circ$ .

As there are but three possible isomerides of the acid  $C^4H^5O^2$ , viz., crotonic acid  $CH^3-CH=CH-CO^2$ , methacrylic acid  $\begin{smallmatrix} H^2C \\ H^2C \end{smallmatrix} \equiv C-CO^2H$ , and the acid  $CH^2=CH-CO^2H$ , the last formula would seem to belong to quarternylic acid; but this acid, when fused with potash, should yield formic and propionic acids (p. 397), whereas according to Geuther, it yields nothing but acetic acid, whence it should have the constitution  $CH^2-CH=CH-CO^2H$ . Its separate existence must, therefore, for the present, be regarded as doubtful.

The neutral oil above mentioned as one of the products of the action of phosphorus pentachloride on ethyl-diacetic acid is, according to Geuther, a mixture of the ethylic ethers of chloroquartenylic and chlorotetraacrylic (chlorocrotonic) acids, which acids may be obtained from it by heating it for several days with strong hydrochloric acid, and distilling the product with water.

According to these results, the action of phosphorus pentachloride on ethyl-diacetic acid gives rise to monochlorocrotonic chloride (or two isomeric chlorides) which is converted into chlorocrotonic acid by treatment with water, and to the corresponding ethylic ether (or two isomeric ethers) thus:



A brown resin is also formed, probably a secondary product.

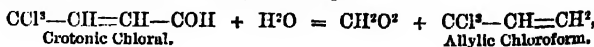
**CROTONIC ALDEHYDE,  $C^3H^4O$ .** The formation of this compound by condensation of 2 mols. acetic aldehyde, under the influence of dehydrating agents has been already explained (pp. 34, 396). The best yield is obtained as follows:—Pure aldehyde is heated in soda-water bottles with very little zinc chloride and a few drops of water for a day or two at  $100^\circ$ . The unchanged aldehyde is then distilled off, and the distillation continued in a current of steam; the residue contains higher condensation-products. The crotonic aldehyde distils over with the steam and partly floats on the water in the receiver, partly dissolves in it; by redistilling the solution, and collecting the first portion apart, the greater part may however be recovered.

It has been stated by Paternò a. Amato that crotonic aldehyde is formed by heating aldehyde with ethyldene chloride (1st Suppl. 513). According to Krämer a. Pinner (*Deut. Chem. Ges. Ber.* iii. 75; *Zeitschr. f. Chem.* [2] vi. 470), no such result is obtained if the ethyldene chloride has been previously purified from phosphorus oxychloride; in the contrary case, however, hydrochloric acid is formed, and acts upon the aldehyde in the manner already explained, producing crotonic aldehyde and other condensation-products.

Crotonic aldehyde is contained in small quantity in the "first runnings" of the distillation of spirit (Krämer a. Pinner, p. 32).

**CROTONIC CHLORAL,  $C^3H^3Cl^2O$ .** *Trichlorocrotonic Aldehyde* (Krämer a. Pinner, *Ann. Ch. Pharm.* clviii. 37).—This compound is formed by the action of chlorine on acetic aldehyde. When chlorine is passed into aldehyde, at first carefully cooled in a freezing mixture, and heated to  $100^\circ$  only at the close of the reaction, the first few bubbles cause the separation of a small quantity of solid metachloral; after a short time, however, evolution of hydrochloric acid sets in and every trace of chlorine is absorbed. The resulting brown mass consists of two layers: a lower, darker, almost solid, and an upper, lighter-coloured liquid layer, the latter being a saturated aqueous solution of hydrochloric acid and the bodies of the lower layer. As it was found impossible to separate these two completely, the whole was submitted to distillation. A considerable quantity passed over between  $90^\circ$  and  $100^\circ$ ; the thermometer then rose rapidly to  $160^\circ$ ; and the main product distilled over between this point and  $180^\circ$ ; the temperature then rose to about  $210^\circ$ , but only decomposition-products were obtained, and a considerable carbonaceous residue remained in the flask. The portion which passed over between  $160^\circ$  and  $180^\circ$  yielded by systematic fractional distillation a liquid boiling between  $163^\circ$  and  $165^\circ$  and having the composition of crotonic chloral,  $C^3H^3Cl^2O$ . The formation of this compound is easily explained. By the first action of chlorine on aldehyde, hydrochloric acid is produced; and this acid, reacting on the aldehyde in the manner already explained (p. 34), converts it into crotonic aldehyde,  $C^3H^4O$ , which then, by the further action of the chlorine, is gradually converted into crotonic chloral.

Crotonic chloral is a colourless oil of peculiar odour, somewhat recalling that of ordinary chloral; it combines with water, forming a crystalline hydrate, the reaction being attended with considerable rise of temperature; on mixing it with alcohol, much heat is evolved, but no crystalline compound is formed. Fuming nitric acid converts it into trichlorocrotonic acid  $C^3H^2Cl^3O^2$ . In short, in chemical behaviour, it corresponds in every respect with the trichloraldehyde of the acetic series, excepting in its reaction with alkalis. Ordinary chloral treated with alkalis yields formic acid and chloroform, and therefore crotonic chloral might be expected to yield formic acid and allylic chloroform,  $C^3H^3Cl^2$ , according to the equation:



instead of this, however, it yields dichlorallylene,  $C^3H^2Cl^2$  or  $CCl^2=C=CH^2$ , the alkali removing a molecule of hydrogen chloride (Krämer a. Pinner).

When crotonic chloral is digested with aqueous *hydrocyanic acid* in a vessel having a condenser attached to it, the cyanhydrin,  $CCl^3-CH=CH-CH \begin{smallmatrix} OH \\ CN \end{smallmatrix}$ , is formed by direct addition, and this compound, by prolonged digestion with strong hydrochloric acid, is converted into trichloroangelic acid,  $CCl^3-CH=CH-CH \begin{smallmatrix} OH \\ CO^2H \end{smallmatrix}$ , a solid substance melting at  $40^\circ$  (Bischoff a. Pinner, *Deut. Chem. Ges. Ber.* v. 208).

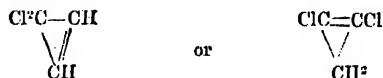
*Crotonic Chloralhydrate*,  $CCl^3-CH=CH-CH \begin{smallmatrix} OH \\ OH \end{smallmatrix}$  may be easily recrystallised from water, forming thin, dazzling white, shining plates, which pertinaciously retain water and melt at  $78^\circ$ . It is very volatile in a current of steam. It is difficultly soluble in cold, readily in hot water, very soluble in alcohol. Its vapour powerfully attacks the mucous membrane and the eyes. When heated it seems to



split up into water, carbon monoxide, hydrogen chloride, and dichlorallylene (Kramer a. Pinner).

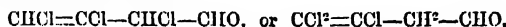
The constitution of crotonic chloral is not quite settled. From the mode of formation, as above explained, it would seem to be that which is represented by the formula  $\text{C}^1\text{H}^2=\text{CH}^3-\text{CHO}$ . Pinner, however (*Deut. Chem. Ges. Ber.* v. 205), from the behaviour of the dichlorallylene obtained from it, infers that it has a different constitution. When this dichlorallylene is treated with bromine,  $\text{Br}^2$  is first taken up and then  $\text{Br}$  is substituted for  $\text{H}$ , yielding a derivative, not of propane,  $\text{C}^3\text{H}^6$ , but only of propylene,  $\text{C}^3\text{H}^4$ . Dichlorodibromopropylene  $\text{C}^3\text{H}^2\text{Cl}^2\text{Br}^2$ , thus produced by addition of  $\text{Br}^2$ , is converted by alcoholic potash into dichloromonobromallylene,  $\text{C}^3\text{H}^2\text{Cl}^2\text{Br}$ , and this body takes up  $\text{Br}^2$  and no more, yielding crystalline dichlorotribromopropylene  $\text{C}^3\text{H}^2\text{Cl}^2\text{Br}^3$ , from which alcoholic potash removes, not  $\text{HBr}$ , but the  $\text{Br}^2$  just added, reproducing dichloromonobromallylene; and by digesting the dichlorotribromopropylene with bromine at  $160^\circ$  in a sealed tube, the last hydrogen atom is replaced, and dichlorotetrambromopropylene  $\text{C}^3\text{H}^2\text{Cl}^2\text{Br}^4$  is formed. In all this series of reactions only propylene derivatives are produced. Impure crotonic chloral, however, when treated with potash, yields—besides dichlorallylene—trichloropropylene  $\text{C}^3\text{H}^2\text{Cl}^3$ , which takes up  $\text{Br}^2$ , forming a propane derivative,  $\text{C}^3\text{H}^2\text{Cl}^3\text{Br}^2$ , and is converted, by caustic potash, into dichlorallylene.

From these reactions Pinner infers that dichlorallylene has a constitution represented by an annular formula :



that the trichloropropylene which is converted into dichlorallylene by potash, is either  $\text{CHCl}=\text{CCl}-\text{CH}^2\text{Cl}$ , or  $\text{CCl}^2=\text{CCl}-\text{CH}^2$ ;

and that crotonic chloral is either—



**CROTONITRIL**,  $\text{C}^4\text{H}^5\text{N}$ . Syn. with ALLYL CYANIDE. See CYANIDES.

**CROTONYLENE**,  $\text{C}^4\text{H}^6$ . This hydrocarbon, originally obtained by Caventon by the action of sodium ethylate on butylene bromide (p. 224), has the constitution of ethyl-acetylene,  $\text{HC}\equiv\text{C}-\text{CH}^2\text{CH}^3$ , inasmuch as its tetrabromide  $\text{C}^4\text{H}^2\text{Br}^4$ , is identical in properties with that which is formed by the action of bromine on ethyl-acetylene synthetically prepared by passing a mixture of acetylene and ethylene through a tube heated to low redness. The tetrabromide melts at  $113^\circ-115^\circ$ . Crotonylene is also produced by the action of a low red heat on the hydrocarbons obtained from petroleum (Prunier, *Compt. rend.* lxxvi. 1410).

*Crotonylene dichloride*,  $\text{C}^4\text{H}^4\text{Cl}^2$ , is formed by the action of phosphorus pentachloride on crotonic aldehyde. It is a colourless liquid, boiling at  $125^\circ-127^\circ$ , and having a specific gravity of 1.131 at  $20^\circ$ . It is decomposed by alcoholic potash, but no definite products of the reaction have yet been obtained (Kokulé, *Ann. Ch. Pharm.* clxii. 98).

*Tetrachloro-crotonylene*,  $\text{C}^4\text{H}^2\text{Cl}^4$ , is obtained by heating crotonic chloral to  $110^\circ-120^\circ$  with phosphorus pentachloride, and subjecting the resulting liquid, which boils between  $130^\circ$  and  $140^\circ$ , to fractional distillation (Judson, *Zeitschr. f. Chem.* [2]. vii. 40).

**CROTYL ETHERS**. *Isocrotyl Bromide*,  $\text{C}^4\text{H}^7\text{Br}$  =  $\text{C}(\text{CH}^3)^2=\text{CHBr}$ , is produced by heating isobutylene bromide with alcoholic potash (p. 224). It is a colourless, heavy, aromatic liquid, insoluble, or nearly so, in water, boiling at  $88^\circ-92^\circ$ . Heated in sealed tubes to  $160^\circ$  with concentrated alcoholic potash, or crystallised sodium ethylate, it is converted, by exchange of  $\text{Br}$  for  $\text{OC}^2\text{H}^5$ , into ethyl-isocrotyl ether  $(\text{C}^2\text{H}^5)(\text{C}^4\text{H}^7)\text{O}$ , or  $\text{C}(\text{CH}^3)^2=\text{CHOC}^2\text{H}^5$ , which, when precipitated by water, and purified by fractional distillation, forms a colourless mobile liquid, lighter than water, boiling at  $92^\circ-94^\circ$ , having a peculiar but not irritating odour resembling that of common ether and that of the distillation-products of the fats. Heated to  $100^\circ$  with fuming hydriodic acid, it yields ethyl iodide. It does not attack ammoniacal silver solution or unite with sodium bisulphite, but unites energetically with bromine, forming the compound  $\text{C}^4\text{H}^7\text{Br}^2\text{O}$  (Butlerow, *Zeitschr. f. Chem.* [2] vi. 523).

**CRYPTOPINE**. See OPIUM ALKALOIDS.

**CRYSTALLINE DISSOCIATION**. See CHEMICAL ACTION (pp. 202-304).

**CRYSTALLISATION**. Observations on the crystallisation of several metallic oxides from fusion with borax and microcosmic salt have been made by Knop (*Ann. Ch. Pharm.* clvii. 363; clix. 36). See TRN. TITANIUM, and ZIRCONIUM.  
2nd Sup.

**CUBEBENE**,  $C^{12}H^{22}$ , heated to  $280^{\circ}$  with 56 parts of highly concentrated hydriodic acid, yields pentane,  $C^5H^{12}$ , decane  $C^{10}H^{22}$ , pentadecane  $C^{15}H^{32}$ , and an oil volatilising at about  $360^{\circ}$  (Berthelot, *Bull. Soc. Chim.* [2], xi. 3).

**CUBEBIC ACID**. This name is given to a resinous acid first obtained by Bernatzik (*Chem. Centr.* 1864, 191) from the ethereal extract of cubeb. The extract, after being freed from volatile oil by distillation with water, was dissolved in weak spirit; the solution, mixed with a little potash, was precipitated with barium chloride; and the resulting barium salt, purified by recrystallisation from water, was decomposed by sulphuric acid. Cubebic acid was thus obtained as an easily fusible resin, insoluble in water and acids, easily soluble in alcohol, chloroform and ether, and forming, with the alkalis, neutral salts soluble in water and precipitated by the salts of the alkaline earths and heavy metals.

C. F. Schulze (*Arch. Pharm.* [3], ii. 388) prepares cubebic acid by saponifying the alcoholic extract of cubeb with caustic soda, leaving the resulting soap-cake to itself for some time till crystals of sodium cubebate separate from it, converting this salt into the corresponding lead salt, and decomposing the latter with sulphuretted hydrogen. The filtered solution, when evaporated, left the cubebic acid as a resinous mass which could not be made to crystallise from any solvent.

Cubebic acid thus prepared was found to have the composition  $C^{11}H^{14}O^4$  (according to E. A. Schmidt, *Arch. Pharm.* [2], xli. 1) Heft, its formula is  $C^{11}H^{14}O^7$ . The sodium salt has the composition  $C^{11}H^{13}NaO^4 + 2H^2O$ . The acid melts at  $45^{\circ}$ ; cannot be sublimed; gives with sulphuric acid a crimson colour, which disappears on dilution, and changes to brown on addition of nitric acid. The aqueous solution gives precipitates with the salts of the alkaline earths and heavy metals.

The aqueous solution of the soap gave, on treatment with alcohol, a fatty oil and cubebene; and the residue, treated with hydrochloric acid, yielded a brown resin (Schulze).

**CUCUYOS**. The luminous organs of the Mexican cucuyos have been analysed by C. Heisemann (Pflüger's *Archiv. f. Physiologie*, vii. 365). The organs, after being carbonised at a low heat, were treated with boiling water. The water was found to contain phosphoric acid and potash, also traces of chlorine, and on the addition of hydrochloric acid, a gas was given off, whose nature could not be determined, owing to the small quantity. The residue, insoluble in water, was almost entirely soluble in hydrochloric acid, and gave distinct evidence of carbonic acid and lime.

Uric acid occurs in these organs in two combinations, first as calcium urate, forming the granular masses; and secondly, as potassium urate, which is referred to the crystalline portion. The carbonic acid contained in the insoluble ash-residue may be regarded as the product of combustion of the uric acid, and the phosphoric acid is, probably, derived from the luminous cells; but the important question whether it occurs preformed and combined with potash, or is produced by the combustion of organic bodies containing phosphorus, remains as yet undecided.

**CUMENE**,  $C^9H^{12}$ . Determinations of the specific gravity of cumene, prepared by distilling cumic acid with lime, have lately been made by Pisanti a. Paternò (*Gazzetta chimica italiana*, iii. 574), with the following results:

Temperature	$0^{\circ}$	$25^{\circ}$	$50^{\circ}$	$75^{\circ}$	$100^{\circ}$
Specific gravity	0.87976	0.85870	0.83756	0.81555	0.79324

Coefficient of Expansion =  $0.90096302 + 0.0000010218t + 0.00000002297t^2$ .

Observations on the xylenes and cumenes of coal-tar naphtha have been made by Rommieu (*Compt. rend.* lxx. 641). Coal-tar naphtha, boiling between  $130^{\circ}$  and  $200^{\circ}$ , was dissolved in sulphuric acid, the solution partially saturated with soda and then distilled. The mass gradually carbonised, swelled up and yielded a distillate consisting of two liquid layers, together with torrents of sulphur dioxide. The lower layer consisted of acid water, the upper of a compound (?) of sulphurous acid and several homologues of benzene, easily decomposable by sodium carbonate. The hydrocarbons thus separated boiled between  $130^{\circ}$  and  $200^{\circ}$ . Of 12 litres of these hydrocarbons, 10 litres dissolved in sulphuric acid, and the solution, when distilled, yielded 2.7 litres of a liquid which gave by fractional distillation 350 c.c. of a hydrocarbon boiling at  $130^{\circ}$ – $140^{\circ}$ , and having the composition of xylene; 150 c.c. boiling at  $165^{\circ}$ – $167^{\circ}$ , and having the composition of cumene, and 200 c.c. of a liquid boiling at  $170^{\circ}$ – $200^{\circ}$  which was not further examined. The xylene thus obtained is said by Rommieu to yield, with fuming nitric acid, a dinitroxylene different from that which is obtained from xylene not previously treated with sulphuric acid. The two dinitrocumenes melt at  $86^{\circ}$  [which is the melting point of dinitromesitylene (*1st Suppl.* 299)]; but whereas ordinary cumene, or mesitylene (?), requires only 4 to 5 times its weight of nitric acid

to convert it into the dinitrocompound, the cumene separated from the sulphuric acid compound is not completely converted into dinitrocumene, even by 20 times its weight of the fuming acid. According to measurements by Descloizeaux (*Compt. rend.* lxx. 587) the two dinitroxylenes and the two dinitrocumenes exhibit differences in their crystalline forms.

**CUMIC ACID**,  $C^{10}H^{12}O^2 = C^6H^4.C^4H^2.CO.OH$ . To prepare this acid from Roman cumin oil, Beilstein a. Kupffer (*Deut. Chem. Ges. Ber.* vi. 1184) proceed as follows: The oil is dropped through a tap-funnel on potassium hydrate melted in an iron pot like those used in the preparation of ammonia. Into the lid of this pot is fitted a Wurtz's boiling tube, the lateral tube of which is connected with a condenser. When the evolution of hydrogen has ceased, water is poured into the pot, and the cumene is distilled off. The alkaline solution is precipitated with hydrochloric acid, and the filtrate thrown away, as cumic acid is but very slightly soluble in cold water. By combining the cumic acid with lime and decomposing the resulting salt with hydrochloric acid, the cumic acid is easily obtained pure, with the melting point  $114^{\circ}$  ( $115^{\circ}$  according to Gerhardt).

**Barium Cumate**,  $Ba(C^{10}H^{11}O^2)^2 + 2H^2O$ , forms nacreous tabular laminæ, which give off their water over sulphuric acid: 100 parts of water at  $20.5^{\circ}$  dissolve 0.810 part of the anhydrous salt.

**Calcium Cumate**,  $Ca(C^{10}H^{11}O^2)^2 + 5H^2O$ , forms hemispherical tufts of needles having a silky lustre; effloresces very readily in the air; gives off  $2H^2O$  over sulphuric acid.

**Magnesium Cumate**,  $Mg(C^{10}H^{11}O^2)^2 + 6H^2O$ , forms thin, tabular, nacreous laminæ, which do not give off water over sulphuric acid: 100 parts of water at  $20.5^{\circ}$  dissolve 0.825 part of the anhydrous salt.

**Bromocumic acid**,  $C^{10}H^{11}BrO^2 = C^6H^4.C^4H^2.Br.CO.OH$ , is formed by heating cumic acid with hydrobromic acid and bromine in a sealed tube for two hours to  $120^{\circ}$ . It may be crystallised from light petroleum oil, and is very apt to creep over the sides of the containing vessel in crystals. When boiled with alcoholic potash, it yields chiefly oxethyl-cumic acid  $C^6H^4.C^4H^2.O.C^2H^3.CO^2H$ , oxycumic acid  $C^6H^4.C^4H^2.OH.CO^2H$  being, however, formed at the same time. The brominated acid heated in a stream of carbon dioxide gives off hydrogen bromide and yields allyl-phenyl-formic acid: the barium salt has the composition  $C^{20}H^{18}BaO^4 + H^2O$  (Czampelik, *Deut. Chem. Ges. Ber.* 1870, 476).

**CUMIDIC ACID**,  $C^{10}H^{10}O^4$ , and **CUMYLIC ACID**,  $C^{10}H^{12}O^2$ , are produced by oxidation of durene or tetramethyl-benzene (1st Suppl. 828).

**CUPRITE**. Native cuprous oxide. See COPPER (p. 389).

**CURARINE**. Curarine gives with sulphuric acid and potassium dichromate a blue-violet tint, not unlike that produced by strychnine under the same circumstances, but more permanent; the brown colouring matters apt to be present in crude curarine interfere much with the reaction; neither precipitation by lead acetate nor treatment with animal charcoal is sufficient to purify an alkaloid thus contaminated.

Curarine extract (best prepared by means of glycerin) yields an amorphous precipitate of curarine chromate with potassium-dichromate (neutral chromate does not answer so well): this precipitate is more soluble in water than the corresponding strychnine compound, which, moreover, is crystalline; when air-dry, it dissolves in sulphuric acid with a pure and deep blue colour, whereas the strychnine salt gives a violet tint; in neither case could the colouring matter be separated and examined by itself. Phosphoric acid cannot be substituted for sulphuric acid in this reaction.

Potassio-mercuric iodide and potassium platinoeyanide precipitate curarine from its glycerin solution, as amorphous flakes, which do not become crystalline when dissolved in alcohol, and separated from this solution; the corresponding strychnine compounds readily become crystalline by this treatment.

Curarine may be separated from strychnine by means of benzene, in which the former is insoluble; it is readily soluble in water (Flückiger, *N. Repert. Pharm.* xxii. 65).

On the detection of curarine in the animal body, see Koch (*Chem. Centr.* 1871, 219; *Chem. Soc. J.* [2], ix. 600); also Salomon (*Zeitschr. anal. Chem.* x. 451; *Chem. Soc. J.* [2], x. 331).

**CURCUMIN**,  $C^{20}H^{16}O^2$  (F. Daube, *Deut. Chem. Ges. Ber.* iii. 609). The substance hitherto described as the colouring matter of turmeric is a mixture of different resins with the pure compound, which may be obtained in the crystalline state by passing a strong current of steam over coarsely powdered turmeric, to remove the essential oil, washing the residue with hot water as long as colouring matter is extracted, then

drying it, and treating it with boiling benzene. On cooling, crude curcumin separates in crystalline crusts, which must be pressed between filtering paper and dissolved in cold alcohol, a small quantity of a yellow body being left behind. To the filtrate a solution of neutral lead acetate is added, and then so much basic acetate that the solution just shows a faint acid reaction. The brick-red precipitate, after being washed, is suspended in water and decomposed by sulphuretted hydrogen. From the precipitate the curcumin is extracted with boiling alcohol, and the solution allowed to evaporate very slowly.

Pure curcumin crystallises in shining prisms, apparently belonging to the orthorhombic system, and appearing of a hock or amber colour by transmitted light, orange-red by reflected light. The alcoholic solution is fluorescent, like tincture of turmeric; the spectrum of the reflected light does not show any alteration from the red end to F, but the blue, violet, and ultra-violet portions are replaced by a greyish green band, in which the lines H, L, M, N, &c., are distinctly visible. By analysing this modified spectrum with a prism it was found to contain very little red, and the blue end had nearly disappeared. This secondary spectrum agrees very nearly with that of uranium glass.

Curcumin begins to melt at 165°, and is completely decomposed at a higher temperature. It is very readily soluble in alcohol and ether, but these solvents cannot be used for extracting it from turmeric, as they also dissolve resinous matters. In benzene it is very little soluble (1 part in 2,000 parts), but as the resins are quite insoluble in this liquid, it may be used to obtain the pure compound. It is also slightly soluble in concentrated mineral acids, which, however, act on it. In alkalis it dissolves with a bright reddish brown colour; acids precipitate from this solution the original substance; calcium- and barium-salts produce reddish-brown precipitates. The lead-compound, which has a bright red colour, is soluble in acetic acid, and is slowly decomposed by carbonic acid. The analyses of the lead-compound did not give concordant results, but they make the formula  $C^{20}H^{18}PbO^8$  probable.

Hot dilute nitric acid oxidises curcumin to oxalic acid. Sodium-amalgam decolorises the alcoholic solution completely. The colour reactions of pure curcumin are much purer than those of turmeric solution. They are best seen with curcumin paper, prepared with Swedish filter-paper free from lime. Alkalis change the yellow into a brownish red, which, after drying, assumes a violet tinge; dilute acids restore the original yellow. A solution of boric acid produces a pure orange, which appears only after drying; if the paper has been previously dipped in a dilute acid, the coloration becomes darker, as dilute acids alone produce a blackish tinge after drying. The orange colour is not changed by diluted acids, but dilute alkalis convert it into a blue, which soon changes into a dirty grey.

By acting on curcumin with boric acid and concentrated sulphuric acid, E. Schlumberger obtained a substance which he called rosocyanin, as its solution has the colour of a rosaniline salt, and its metallic compounds are blue. Daube has obtained the same results with pure curcumin.

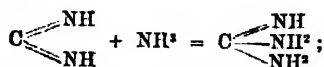
Kachler (*Deut. Chem. Ges. Ber.* iii. 713) believes that he has obtained anthracene by treating impure yellow curcumin with zinc-dust. The action of sodium-amalgam on curcumin gave rise to a number of resinous and syrupy products.

By oxidation with chromic acid mixture, curcumin is converted into terephthalic acid (*J. Gajevsky, Deut. Chem. Ges. Ber.* vi. 196).

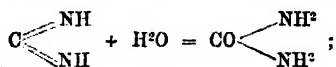
**CYANAMIDE**,  $CN^2H^2$  (E. Mulder, *Deut. Chem. Ges. Ber.* vi. 655). An aqueous solution of this compound yields with ammoniacal silver nitrate a yellow precipitate, which has the composition  $CN^2Ag^2$ , and is reconverted into cyanamide when suspended in water and decomposed by sulphuretted hydrogen. From this Mulder infers that

the formula of cyanamide is, not  $N \equiv C - NH^2$ , as commonly supposed, but  $C \begin{smallmatrix} \nearrow NH \\ \searrow NH \end{smallmatrix}$ ,

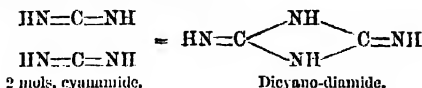
and he proposes to call it carbodiimide or cardimide. It is not easy to see, however, why the simultaneous replacement of the two atoms of hydrogen by silver in cyanamide is more easily explained by the proposed formula than by the ordinary one, inasmuch as the two hydrogen-atoms are similarly placed in the latter as well as in the former. Mulder further points out that the proposed formula of cyanamide affords an easy explanation of the conversion of that compound into guanidine by the action of ammonia (*1st Suppl.* 634):



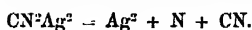
and into urea (regarded as carbamide) by the action of water;



also of its polymerisation to dicyano-diamide :



Silver-carbodiimide or argento-cyanamido is insoluble in water, slightly soluble in ammonia, soluble in dilute nitric acid, and reprecipitated by ammonia or potash. It is not decomposed by boiling with potash, or by exposure to light. It undergoes no change at 220°, but explodes at a higher temperature, with formation of cyanogen



Cyanamide also gives a precipitate with ammoniacal cupric sulphate (Mulder). The silver and copper compounds were described in 1858 by Beilstein & Geuther (ii. 188).

Cyanamide unites with *alanine*, forming a compound called *alacreatine* isomeric with creatine (p. 393). It does not combine with *ethyl carbonate* (*urethane*) when heated with it either in the dry state or in aqueous solution; hence it seems probable that in the formation of creatine from cyanamide and sarcosine, the cyanamide unites with the carboxyl, and not with the amido-group (Baumann, *Ann. Ch. Pharm.* clxvii. 77).

**CYANBENZYLAMIDE** and **CYANBENZYLAMINE**. See BENZYLAMINE (pp. 181, 182).

**CYANETHYLPHOSPHINE**,  $\text{C}^3\text{H}^5\text{NP} = \text{P} \begin{Bmatrix} \text{H} \\ \text{C}^2\text{H}^3 \\ \text{CN} \end{Bmatrix}$ . When an ethereal solu-

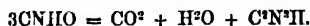
tion of phosphine is heated for some hours to 100° in a sealed tube with cyanogen chloride, and the ether afterwards distilled off, there remains a syrupy liquid which solidifies after a short time over sulphuric acid. This product recrystallised several times from ether yields cyanethyl-phosphine in coherent masses of rhombic plates, which melt at 49°–50°, and dissolve in water, alcohol, and ether. When treated with oxidising agents, it gives off aldehydo (Darmstädter & Henniger, *Deut. Chem. Ges. Ber.* iii. 179, 404).

**CYANIC ACID**. On the action of cyanic acid on chloral, see CHLORAL (p. 310).

According to Rabuteau & Massul (*Compt. rend.* lxxiv. 57), the metallic cyanates are not poisonous; they are converted into carbonates in the animal organism.

On the Heat of Formation of Cyanates, see HEAT.

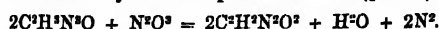
*Potassium Cyanate*.—According to A. Bannow (*Deut. Chem. Ges. Ber.* iv. 253; *Chem. Soc. J.* [2], ix. 391), a salt having the composition of potassium cyanate, but differing from it in some of its properties, is formed by the action of potash on paracyanogen, also by heating the ordinary cyanate with iodide of cyanogen. It crystallises in needles, and its aqueous solution, heated for a long time with alkali, and then neutralised, gives with silver nitrate a white precipitate, unaffected by light, and having the composition  $\text{C}^2\text{N}^2\text{Ag}$ . The reaction may, perhaps, be expressed by the equation :



[If this be correct, the new salt is probably tripotassic cyanurate  $\text{C}^2\text{N}^2\text{K}^3\text{O}^2$ .]

Cahours & Gal (*Bull. Soc. Chim.* [2] xiv. 449) have studied the action of potassium cyanate and cyanic ethers on the ethers of aromatic amido-acids, and have obtained compounds analogous to those prepared by Griess and Menchutkin (*1st Suppl.* 318). To prepare these compounds, an aqueous solution of potassium cyanate is gradually poured into a warm solution of the sulphate of the acid ether; the separated oil, which soon solidifies in the crystalline form, is mixed with water; and the product is crystallised from alcohol or hot water. When an alcoholic cyanate is used, it is mixed with about its own volume of the liquid or fused ether of the amido-acid, and the resulting crystals, after being pressed, are recrystallised from alcohol or ether.

**Dicyanic Acid**,  $\text{C}^2\text{H}^2\text{N}^2\text{O}$  (Poensgen, *Ann. Ch. Pharm.* cxviii. 339).—Formed by the action of nitrous acid on cyanurea suspended in water (p. 417):



It is slightly soluble in cold, more soluble in hot water, and crystallises therefrom in

hard, mostly light yellow monoclinic prisms in which, according to Carius, the angle  $\infty P : \infty P$  in the clinodiagonal principal section is  $79^\circ 36'$ , in the orthodiagonal section,  $100^\circ 10'$ ;  $OP : \infty P$  in front =  $103^\circ 30'$ ; angle of inclined axes =  $68^\circ 20'$ ; ratio of orthodiagonal to clinodiagonal =  $0.772 : 1$ . The crystals contain  $2C^2N^2H^2O^2 + 3H^2O$ ; they effloresce very quickly, and give up their water of crystallisation even when boiled under water. From nitric acid, dicyanic acid crystallises unaltered in long prisms, from hydrochloric acid in green, shining spangles. When heated, it is converted into cyanic acid at the same temperature as cyanuric acid; by boiling with alkalis, it is resolved into carbonic acid and ammonia.

The metallic dicyanates are either neutral or acid; those of the alkali-metals are easily soluble in water; the ammonium salt is crystalline and easily decomposable. The barium salt  $(C^2N^2HO)^2Ba + H^2O$  separates in monoclinic laminae on mixing the ammonium salt with baryta-water; it is also formed on heating cyanurea with barium hydrate. The acid and neutral silver salts  $C^2N^2HAgO^2$  and  $C^2N^2Ag^2O^2$  are white amorphous precipitates, insoluble in water. The neutral salt, treated with ethyl iodide, yields a viscid ether having a peculiar odour.

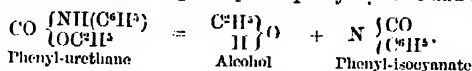
According to Hallwachs (*Zeitschr. f. Chem.* vi. 354), Poensgen's dicyanic acid is nothing but cyanuric acid. It certainly agrees very closely therewith in many of its properties, especially in its crystalline form. (The crystals of cyanuric acid are monoclinic, having the angle  $\infty P : \infty P$  (clinod.) =  $77^\circ 13'$ ;  $OP : \infty P$  =  $99^\circ 59'$ ; ratio of ortho- to clinodiagonal =  $0.772 : 1$  or =  $0.573 : 0.781$ ; see ii. 289). Nevertheless, the existence of amidodicyanic acid and of Hofmann's dicyanic ethers renders the existence of dicyanic acid highly probable. The question, however, can only be decided by a more exact comparison of the salts of Poensgen's acid with the cyanurates.

*Amido-dicyanic or Dicyanamic acid*,  $C^2N^2H^2O = C^2N^2 \begin{smallmatrix} NH_2 \\ HO \end{smallmatrix}$  (Hallwachs, *Ann. Ch. Pharm.* cliii. 293). This acid was originally obtained by boiling dicyanodiamide with a moderately dilute solution of baryta (*1st Suppl.* 518); part of it, however, is resolved during the process into cyanamide and cyanic acid. If a hot saturated solution of baryta or strong potash-ley be used, the products are melamine, cyanamide and cyanic acid, with only a small quantity of amidodicyanic acid. This acid may also be prepared by direct combination of cyanamide  $CN^2H^2$  and cyanic acid  $CNHO$ . The two bodies are mixed in aqueous solution in the proportion of 1 : 2 and left to stand for 24 hours, or mixed dry and heated to  $60^\circ$  in a water-bath.

The free acid, separated from the silver salt by hydrochloric acid, crystallises in groups of small crystals, or in spicular needles. It decomposes at  $100^\circ$ . Its aqueous solution has an acid reaction, dissolves cuprous oxide and barium carbonate, is precipitated by silver nitrate, and decomposed with effervescence by concentrated acids. The ammonium salt forms colourless needle-shaped crystals. The potassium salt  $(C^2N^2H^2KO)$  is easily soluble in water, and crystallises with difficulty; the sodium salt,  $C^2N^2H^2NaO$ , resembles it. The silver salt,  $C^2N^2H^2AgO$ , obtained by precipitation from the potassium salt is a white, amorphous powder, insoluble in water either hot or cold, slightly soluble in dilute nitric acid, easily soluble in ammonia. From hot dilute nitric acid it separates as a heavy crystalline powder; from dilute ammonia, by spontaneous evaporation, in small shining needles. When warm, moderately strong aqueous ammonia is saturated with the silver salt, the solution, on standing, deposits tabular crystals which give off ammonia on exposure to the air. The copper salt,  $(C^2N^2H^2O)^2Cu + 4H^2O$ , forms large sky-blue crystals sparingly in cold, more easily in hot water. The aqueous solution, on boiling, deposits an insoluble dark green powder, having the composition  $C^2N^2H^2CuO + 2H^2O$ , and easily soluble in mineral acids, the solution, on cooling, depositing the original blue salt. Both these copper-salts blacken at  $100^\circ$ , and at a red heat give off vapours containing copper. The barium salt,  $(C^2N^2H^2O)^2Ba + 3H^2O$ , is a white radiate-crystalline mass, very soluble in water, and crystallises from absolute alcohol in small cubic crystals.

**Tricyanic or Cyanuric acid**,  $C^3N^3H^3O^3$ .—*Detection*.—This acid, if present in the free state and in any considerable quantity, is most readily detected by heating the highly dried substance in a short narrow tube. The smell of the vapour of cyanic acid thereby evolved is so characteristic, that there is little room for doubt as to presence or absence of cyanuric acid. To detect this acid when in solution and present in extremely small quantity, advantage may be taken of the sparing solubility of sodium cyanurate in hot concentrated soda-ley. The liquid to be tested is placed in a watch-glass, mixed with strong soda-ley, and warmed for a moment over a pointed flame. If cyanuric acid is present, splendid delicate needles of trisodic cyanurate  $C^3N^3Na^3O^3$  at once make their appearance, spreading from the point at which the flame is applied, and disappearing again as the liquid cools, provided the solution is not too strong. The formula of sodium cyanurate is  $C^3N^3Na^3O^3$  (Hofmann, *Deut. Chem. Ges. Ber.* iii. 601).

**CYANIC, DICYANIC, and CYANURIC ETHERS.** AROMATIC ISO-CYANATES; \* (Hofman, *Proc. Roy. Soc.* xix. 108). *Phenyl Isocyanate* or *Phenylcarbimide*,  $N \begin{Bmatrix} CO \\ C^2H^3 \end{Bmatrix}$ .—This substance, originally obtained by the dry distillation of melonoximide or oxalyl-diphenylguanidine, and afterwards more easily by heating diphenyl-carbamide with phosphoric anhydride (1st *Suppl.* 197), is also produced when ethyl phenyl-carbamate or phenyl-urothane (which Wilm a. Wischin have lately obtained by the action of ethyl-chlorocarbonate on aniline, p. 252) is distilled with phosphoric anhydride, whereupon it splits up into phenyl cyanate and ethyl alcohol.



The alcohol then remains behind, and the isocyanate distils over as a colourless liquid, which may be purified by rectification. It has a very pungent odour, a specific gravity of 1.092 at 15°, and boils at 163° (not at 178° as formerly stated).

With water it yields carbon dioxide and diphenylcarbamide; it unites with alcohols, forming urethanes; and with ammonia and its derivatives it forms various carbamides or ureas. But its most characteristic reaction is with triethylphosphine. On dipping a glass rod moistened with this base into a large quantity of the isocyanate, it becomes very hot and quickly solidifies to a mass of beautiful crystals, consisting of phenyl cyanurate; it is not, however, yet decided which of the isomeric modifications of that compound is hereby produced.

The isocyanates of *tolyl*, *xylyl*, and *naphthyl*, are obtained in like manner by distilling the corresponding urethanes with phosphoric anhydride.

*Tolyl Isocyanate*,  $N \begin{Bmatrix} CO \\ C^2H^3 \end{Bmatrix}$ , is a colourless liquid, boiling at 185°, and showing in all its properties the greatest resemblance to the phenyl compound; triethylphosphine acts on it, however, more slowly.

*Xylyl Isocyanate*,  $N \begin{Bmatrix} CO \\ C^2H^3 \end{Bmatrix}$ , is a colourless, highly refractive liquid, boiling at about 200°, and having only a feeble odour; it exhibits reactions similar to those of the other aromatic isocyanates, but they often require days for their completion.

*Naphthyl Isocyanate*,  $N \begin{Bmatrix} CO \\ C^2H^3 \end{Bmatrix}$ , is a colourless, not very mobile liquid, boiling at about 260°–270°. At the ordinary temperature it is almost odourless, but its vapour has the pungent smell peculiar to the isocyanic ethers. With water, alcohols, and ammonias, it gives the characteristic reactions of that class of bodies, and acts with incomparably greater quickness and precision than the xylyl compound. This is particularly shown in the action of triethylphosphine, which causes the isocyanate of the naphthyl series to solidify almost instantaneously.

**Isodicyanic Ethers**,  $N^2 \begin{Bmatrix} (CO)^2 \\ H^2 \end{Bmatrix}$  (Hofmann, *Deut. Chem. Ges. Ber.* iv. 246).

These ethers are intermediate between the isocyanic and isocyanuric ethers. The *phenylic compound*,  $C^2H^3N^2(CO)^2 = N^2(CO)F(C^2H^3)^2$ , the only one yet obtained, is formed as a crystalline mass when a drop of triethylphosphine is let fall into liquid phenyl isocyanate. It dissolves sparingly in boiling ether, and the solution, on cooling and evaporation, deposits the pure substance in very thin beautiful iridescent plates. All other solvents alter it more or less. It melts at 175° and is thereby distinguished from phenyl isocyanurate (for which it was formerly mistaken), which melts at 260°, and from the normal cyanurate, which melts at 224°. Its molecular weight cannot be determined by the vapour-density, since it does not volatilise unaltered, but is converted, on distillation, into liquid phenyl isocyanate, which, however, after standing for 24 hours, resolidifies so completely that not the faintest smell of the liquid isocyanate remains. This effect appears to be due to the presence of small quantities of the original solid substance carried over with the liquid; and, in fact, the direct addition of crystals to the liquid induces partial solidification.

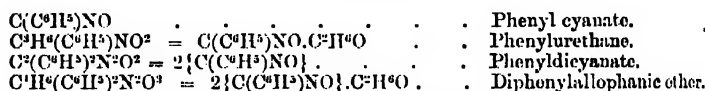
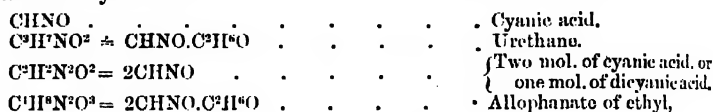
The molecular weight of the compound may, however, be determined by its behaviour with alcohol. On attempting to dissolve the crystals in boiling alcohol, part remains

\* Called 'Cyanates' in the original paper, and in the Abstract given in the *Journal of the Chemical Society* [2] ix. 138. This designation, however, is contrary to analogy; the alcoholic derivatives of cyanic acid,  $N \begin{Bmatrix} (CO) \\ R \end{Bmatrix}$ , formed on the ammonia type, are carbimides or isocyanates, analogous to the carbamides or isocyanides  $N \begin{Bmatrix} C \\ H \end{Bmatrix}$ ; the true cyanic ethers  $C \begin{Bmatrix} N \\ OR \end{Bmatrix}$  are those which are produced by the action of cyanogen chloride on the sodium-alcohols (see 1st Supplement, pp. 319, 322).

for hours undissolved in the boiling liquid, however great an excess of alcohol may be used. Suddenly, however, the liquid becomes clear, and if then left to cool deposits slender needles, which may be purified by one recrystallisation from boiling alcohol. The crystals thus obtained are slightly soluble in ether, insoluble in water, and differ from the original body, not only by their form and their solubility in alcohol, but likewise by their lower melting point (98°). The analysis of these crystals leads to the formula  $C^{10}H^{16}N^2O^2$ , which is that of the ethylic ether of diphenylallophanic acid, containing the elements of 2 mols. phenyl cyanate and 1 mol. ethyl alcohol. It may, therefore, be assumed with great probability that the polymeric cyanate is a diacyanate, and that the crystalline compound just mentioned is formed by combination of 1 mol. of this diacyanate with 1 mol. alcohol:



The isodicyanate, indeed, reacts with alcohols just like the unpolymerised cyanate, which likewise takes up 1 mol. alcohol to form urethane. In whatever way, therefore, we may suppose the elements of the diacyanate to be grouped, it is clear that it is related to the original liquid cyanate in the same manner as Liebig u. Wöhler's ethyl allophanate to cyanic acid.



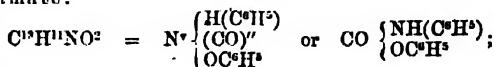
The diphenylallophanic ether splits up, on distillation, into alcohol and phenyl isodicyanate, the latter being almost entirely converted into the simple isocyanate.

*Methylic Diphenylallophanate*,  $2C(C^6H^5)NO.CH^3O$ , easily obtained pure by dissolving phenyl isodicyanate in methylic alcohol and recrystallising from alcohol, forms difficultly soluble needles, which melt at 231°, or 133° higher than the corresponding ethyl compound.

*Amylic Diphenylallophanate*,  $2C(C^6H^5)NO.C^5H^{11}O$ , obtained by dissolving the isodicyanate in amylic alcohol, forms colourless and scentless crystals insoluble in water, easily soluble in ether and alcohol, and melting at 58°. This compound often remains fluid for a long time.

*Sulphuretted Amylic Diphenylallophanate*,  $2C(C^6H^5)NO.C^5H^{11}S$ .—The isodicyanate unites with mercaptans as well as with alcohols. Heated with amylic mercaptan for some hours to 160° it dissolves, and the mixture gradually solidifies to a white crystalline mass which, when recrystallised from alcohol or ether, yields the sulphuretted ether in colourless and scentless needles, which are insoluble in water and melt at 70°.

*Action of Phenol on Phenyl isodicyanate*.—These two substances act on one another at 150°, but the product does not consist of phenylic diphenylallophanate. On digesting the isodicyanate with excess of phenol in ethereal solution for some hours, needles are produced which are slightly soluble in water, easily in alcohol, melt in contact with boiling water and in the dry state at 122°. These crystals consist of phenylic phenylcarbamate:



obviously produced by the splitting up of the isodicyanate into 2 mol. of isocyanate which then unite with 2 mol. of phenol:

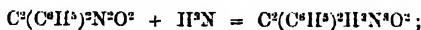


The same result is obtained when only 1 mol. phenol is heated with 1 mol. of the isodicyanate, half of the latter then reappearing as free phenyl isodicyanate and no phenylic diphenylallophanate being formed. The phenylic phenylcarbamate prepared in the manner just described agrees exactly with that which is obtained directly by the action of phenylic isocyanate on phenol.

The molecular weight of phenylic isodicyanate is further corroborated by its reaction



with ammonia. Just as a molecule of alcohol, by uniting with 1 or 2 mols. of cyanic acid, yields respectively urethane or ethylallophanate, so does ammonia by combining with 1 or 2 mols. cyanic acid yield urea or biuret. If, then, the polymerisation of the cyanate in the case under consideration consists in the union of two molecules of cyanate into one, the resulting dicyanate will, by uniting with ammonia and the various amines, give rise to an endless series of alcoholic biurets. Thus, with ammonia, it gives rise to diphenyl-biuret:



and, with aniline, to triphenyl-biuret:



For the description of these compounds see BIURET (p. 193).

**Cyanuric Ethers.** Of these ethers there are two modifications, viz. :—

Normal Cyanurates . . . . .  $C^3 \left\{ \begin{smallmatrix} N^2 \\ (OR)^2 \end{smallmatrix} \right.$

Isocyanurates, or Carbo-triamides . . . . .  $N^3 \left\{ \begin{smallmatrix} (CO)^2 \\ R^2 \end{smallmatrix} \right.$

The isocyanurates, discovered by Wurtz in 1848, are formed by distilling a mixture of potassium cyanate or cyanurate with potassium methylsulphate, ethylsulphate, &c., or by heating silver cyanate with the iodide of an alcohol-radicle (ii. 292). The normal cyanurates are produced by the action of cyanogen chloride on the sodium alcohols, &c. Cloez, in 1857, by acting on sodium ethylate with gaseous cyanogen chloride, obtained a compound isomeric with ethyl cyanate, which he called cyanetholine. Subsequently, in 1866, he obtained the corresponding methyl-compound, though in an impure state, and showed that both these compounds are resolved by heating with potash, into methyl or ethyl alcohol, and cyanuric acid. H. Gal also found (*Compt. rend.* lxi. 527) that cyanetholine, treated with gaseous hydrochloric or hydrobromic acid, yields cyanuric acid and chloride or bromide of ethyl. Nevertheless, these compounds were regarded both by Cloez and by Gal as normal cyanic ethers, CNOR (1st Suppl. 519), and their true molecular weight was first established by Hofmann & Olshausen (*Proc. Roy. Soc.* xviii. 493), who obtained the methyl and phenyl compounds in the pure state.

**Methyl Cyanurate**,  $C^3 \left\{ \begin{smallmatrix} N^2 \\ (OCH^3)^2 \end{smallmatrix} \right.$  or  $\left\{ \begin{smallmatrix} (CN)^2 \\ (CH^3)^2 \end{smallmatrix} \right\} O^2$ .—When gaseous cyanogen chloride is passed into a dilute solution of sodium methylate in methyl alcohol till the liquid smells strongly of it, sodium chloride separates out, and after the methyl alcohol has been distilled off, there remains a brown oil which often retains the liquid form for a long time, but ultimately solidifies. Sometimes, again, little or no oil is formed, but on distilling off the methyl alcohol, there remains a brown crystalline mass which may be purified by recrystallisation from hot water, and treatment with animal charcoal. From the purified mass ether extracts the methyl cyanurate, leaving undissolved rhombic tablets consisting of dimethyl amidocyanurate.

Methyl cyanurate crystallises from alcohol, or better from hot water, in slender needles, melts at 132°, boils between 160° and 170°, but appears to be converted, by distillation, into the isocyanurate, which melts at 175°. Before distillation it is resolved, by heating with potash, into cyanuric acid and methyl alcohol; but after distillation into carbon dioxide and methylamine.

**Dimethyl Amidocyanurate**,  $C^3H^4N^4O^2 = C^3N^3 \left\{ \begin{smallmatrix} OCH^3 \\ NH^2 \end{smallmatrix} \right.$ , is formed, together with several

other compounds, by the action of ammonia on methyl cyanurate, but is more easily obtained as a secondary product in the preparation of the cyanurate, constituting in fact, the rhombic tables above mentioned. It crystallises from hot water in beautiful rhombic tables which melt at 212°, dissolve sparingly in cold water and cold alcohol, and are nearly insoluble in ether. Silver nitrate added to its solution in nitric acid throws down the silver salt  $C^3H^4N^4O^2.AgNO^3$ , which crystallises in beautiful needles.

In preparing methyl cyanurate from somewhat impure methyl alcohol, Cloez once obtained a crystalline substance, which he called *methylantoin*, and to which he assigns the composition of *dimethyl-allantoin*  $C^4H^6N^4O^3$  (1st Suppl. 520). Hofmann (*Compt. rend.* lxxi. 35) suggests that this substance was probably a mixture of methyl cyanurate and dimethyl amidocyanurate.

**Ethyl Cyanurate**,  $C^3N^3(OC^2H^5)^2$ , has not been obtained in the pure state. The action of cyanogen chloride on sodium ethylate goes on in the manner described by Cloez; the resulting liquid deposits variable mixtures of crystals consisting essentially of the ethylic ethers of amido- and diamido-cyanuric acids.

*Diethyl Amidocyanurate*,  $C^2N^3 \begin{cases} OC^2H^4 \\ OC^2H^3 \\ NH^2 \end{cases}$ , is obtained from the crude crystals by treat-

ment with animal charcoal, and repeated crystallisation from water, in delicate white prisms, which melt at  $97^\circ$  and are soluble in alcohol and ether. It is also produced when crude cyanetholine is heated for some hours in a sealed tube with aqueous ammonia. With silver nitrate, it forms the two compounds,  $2C^2H^3N^3O^2 \cdot AgNO^3$ , and  $C^2H^2N^3O^2 \cdot AgNO^3$ .

*Ethyl Diamidocyanurate*,  $C^2N^3 \begin{cases} OC^2H^3 \\ NH^2 \\ NH^2 \end{cases}$ , separates from a solution of the preceding

compound mixed with strong aqueous ammonia, after standing for some time, in white crystals, melting between  $190^\circ$  and  $200^\circ$ , very slightly soluble in alcohol. With silver nitrate it forms a compound which crystallises in slender needles.

The composition of these amidated ethers shows clearly that the compounds formed by the action of cyanogen chloride on the sodium alcohols, are really cyanurates and not cyanates.

*Amyl Cyanurate*.—The product of the action of cyanogen chloride on sodium amylate, resembles cyanetholine. It distils at  $200^\circ$ , apparently with decomposition.

*Phenyl Cyanurate*.— $C^2N^3(OC^2H^3)^3$ . Cyanogen chloride acts on phenol, forming an oil which at first yields phenol by distillation; the later portions of the distillate, however, solidify, and on leaving the whole to cool, washing the residue of the distillation with alcohol, and crystallising from a large quantity of hot alcohol, the phenyl cyanurate is obtained in long slender needles, melting at  $224^\circ$ , nearly insoluble in water and ether, soluble in benzene.

**CYANIDE OF HYDROGEN.** The formation of this compound by the direct union of acetylene and nitrogen (*1st Suppl.* 35, 520), may be easily demonstrated by taking advantage of the property of nearly all hydrocarbons to yield acetylene when a series of electric sparks is passed through their vapours. On passing nitrogen into benzene, exposing the gas charged with the hydro-carbon to the action of the electric spark, and then passing it into silver nitrate, the formation of hydrocyanic acid becomes evident in a few seconds. The same result is obtained when the spark is passed through a mixture of ammonia gas and ether-vapour, not, however, when nitrogen is used instead of ammonia, although acetylene is formed in this case also (Perkin, *Chem. News*, xxi, 66).

*Formation from Nitro-compounds*.—The formation of hydrocyanic acid from picric acid by the action of baryta-water, was pointed out by Wöhler in 1828. The same result is obtained with caustic potash-solution. Dinitrobenzene is also decomposed with production of hydrocyanic acid, by boiling with aqueous potash or soda, and mononitrobenzene is similarly acted upon by the alkaline hydrates in the state of fusion (Post and Hübner, *Deut. Chem. Ges. Ber.* v. 408).

Respecting the quantities of heat evolved or absorbed in the formation and decomposition of hydrogen cyanide, see **HEAT**.

*Spontaneous decomposition of Aqueous Hydrocyanic acid*.—A quantity of aqueous hydrocyanic acid having been left in a glass cylinder merely covered with a funnel and a glass plate, till the liquid had evaporated, a solid residue was found at the bottom, consisting partly of brown amorphous matter, partly of yellowish crystals, which in form, taste, reaction with mercuric nitrate, mercuric chloride and potash, &c., exhibited all the characters of urea (Campani, *Gazzetta chimica italiana*, i. 472).

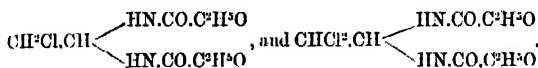
*Action of Chlorine*.—Wurtz, by passing chlorine into dilute hydrocyanic acid, obtained a product which he regarded as a hydrocyanide of cyanogen chloride  $2CNCl$ .  $CNH$  (ii. 218). According to Naumann u. Vogt, however (*Deut. Chem. Ges. Ber.* iii. 523), this product is not a definite compound, but only a mixture of cyanogen chloride and hydrogen cyanide. This conclusion is inferred from the vapour-densities of a product prepared according to Wurtz's directions, and containing a quantity of chlorine (45.4 p.c.) nearly corresponding with the formula  $2CNCl.CNH$ . The observed vapour-densities were 1.65 at  $0^\circ$ , 1.66 at  $12^\circ$ , 1.64 at  $16^\circ$ , and 1.67 at  $100^\circ$ . The formula above-mentioned requires 1.67; a mixture prepared exactly according to the formula would require 1.73; the chemical compound requires 6.18.

Stenhouse described a crystalline compound  $C^2H^{14}Cl^2N^2O^4$ , obtained by passing chlorine gas into a mixture of strong aqueous hydrocyanic acid and alcohol, or into an alcoholic solution of mercuric cyanide (ii. 218). C. Bischoff, on the other hand (*Deut. Chem. Ges. Ber.* iii. 760; v. 80), finds that the dichlorinated compound is produced in the latter case only, but that when chlorine is passed into a mixture of hydrocyanic acid and alcohol, the product mostly consists of the monochlorinated compound  $C^2H^{14}ClN^2O^4$ . This latter closely resembles Stenhouse's compound. It crystallises in white silky

needles, longer and softer than those of the dichlorinated compound; melts at  $147^{\circ}$ ; dissolves easily in ether and alcohol, also in warm nitric acid, from which it is precipitated by water. It is insoluble in hydrochloric acid; sulphuric acid dissolves it, with evolution of heat, forming a yellow solution, and on heating this liquid, the compound is broken up, alcohol and carbon dioxide being eliminated, with simultaneous formation of ammonium sulphate and sulphur dioxide. Potash, soda, and baryta, likewise resolve the compound, when heated with it, into alcohol, carbon dioxide, and ammonia. Heated to  $150^{\circ}$  with alcoholic ammonia, it yields a mixture of organic bases not yet investigated. Digested with hydrochloric acid for 24 hours at  $100^{\circ}$ , it forms ethyl chloride and carbon dioxide, which escape on opening the tubes, and glycolic chlorhydrin and other glycol-compounds, which remain dissolved in the aqueous hydrochloric acid.

These modes of decomposition suggest the following view of the formation of the compound.

It is well known that chlorinated acetals are formed by the action of chlorine on aqueous alcohol, and that urethane is produced by cyanogen chloride under similar circumstances, so that when both reactions take place simultaneously, compounds are formed in which the chloretethylidene group is combined with the urethane residue in place of the alcohol residue (ethoxyl) in chlorinated acetal, namely--



This view readily accounts for the splitting up of the chlorinated compound into alcohol, carbonic acid, and ammonia, and also for the formation of glycol-compounds. The attempts to obtain the corresponding compounds in other series were fruitless, chlorinated acetones and methyl-urethane being obtained with methyl alcohol, whilst amyl alcohol yielded amyl urethane.

When a slight excess of bromine is added to an alcoholic solution of hydrocyanic acid, and the mixture is gently heated, a violent reaction ensues, cyanogen bromide volatilising, and ammonium bromide separating from the solution. On addition of water, an oil separates, which consists chiefly of a solution of the bromine-compound in ethyl bromide, and leaves the former on being allowed to evaporate spontaneously. Bischoff only once obtained the monobrominated compound  $\text{C}^2\text{H}^{12}\text{BrN}^2\text{O}^4$ , which melts at  $142^{\circ}$ , and crystallises in larger needles than the easily prepared dibrominated compound. The dibrominated compound  $\text{C}^2\text{H}^{14}\text{Br}^2\text{N}^2\text{O}^4$  melts at  $115^{\circ}$ – $116^{\circ}$ , and crystallises from ether in long needles.

Iodine, alcohol, and hydrocyanic acid gave a negative result, as did also the digestion of the bromine-compound with potassium iodide. Neither the chlorine- nor the bromine-compound is altered by the action of nascent hydrogen.

On the reaction of hydrocyanic acid with *Chloral* and *Crotonic Chloral*, see pp. 310, 400.

On the detection of hydrocyanic acid, see *ALMEN* (*Chem. Centr.* 1872, 442; *Chem. Soc. J.* [2], xi. 93).

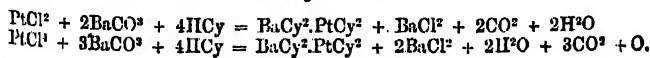
**Polymeride of Hydrocyanic acid.** When a mixture of equal parts of anhydrous hydrogen cyanide and epichlorhydrin is heated in sealed tubes for a fortnight to  $40^{\circ}$ – $60^{\circ}$ , a solid body is formed, which, after treatment with ether and recrystallisation from water and alcohol, is obtained in reddish-brown crystals, the analysis of which has not given concordant results. Treated with baryta-water, it yields ammonia, barium carbonate, and a crystalline body having the composition and properties of glycocine, whence it may be inferred that the original substance is a polymeride of hydrocyanic acid:



(O. Lange, *Deut. Chem. Ges. Ber.* vi. 99).

**CYANIDES, ALCOHOLIC.** See the several radicles, *ALLYL*, *METHYL*, *PROPYL*, *ETHYLENE*, *NAPHTHALENE*, &c.

**CYANIDES, METALLIC.** Weselsky (*Zeitschr. f. Chem.* [2] vii. 61) prepares double cyanides, containing barium, the platinum compounds, for example, by passing a stream of gaseous hydrogen cyanide through a mixture of barium carbonate and a salt of another metal: e.g.



In this manner the following salts have been obtained:—

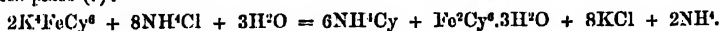
1. *Barium-silver cyanide*,  $\text{BaCy}^2.2\text{AgCy} + \text{H}^2\text{O}$ . This salt, prepared from barium carbonate and silver carbonate, forms warty crystalline masses, which lose their water at  $100^\circ$ . 2. *Barium-zinc cyanide*,  $\text{BaCy}^2.\text{ZnCy}^2 + 2\text{H}^2\text{O}$ , obtained from barium carbonate and zinc sulphate, forms large colourless crystals easily decomposed by exposure to the air. 3. *Barium-palladium cyanide*,  $\text{BaCy}^2.\text{PdCy}^2 + 4\text{H}^2\text{O}$ . This salt, already described by Rossler (1st Suppl. 536), is formed from barium carbonate and palladium cyanide. 4. *Barium-nickel cyanide*,  $\text{BaCy}^2.\text{NiCy}^2 + 3\text{H}^2\text{O}$ . This well-known salt was prepared by the above-described method from nickel sulphate. 5. *Barium-cuprous cyanide*,  $\text{BaCy}^2.\text{Cu}^2\text{Cy}^2 + \text{H}^2\text{O}$ , prepared in like manner, forms large colourless crystals, which are decomposed by exposure to the air. A salt crystallising in fine needles is obtained from the mother-liquors. 6. *Barium-cadmium cyanide*,  $2\text{BaCy}^2.3\text{CdCy}^2 + 10\text{H}^2\text{O}$ , obtained from cadmium sulphate, crystallises well, but is very readily decomposed.

On the Cobaltcyanides prepared in like manner, see 1st Suppl. 536.

**Ferrocyanides** (Wyruboff, *Ann. Chim. Phys.* [4], xvi. 280; xxi. 271). The salts were generally prepared by saturating hydroferrocyanic acid with the other corresponding oxides or carbonates. To obtain the easily soluble salts in distinct crystals the crystallising vessel containing the warm concentrated solution was covered with a sheet of filtering paper, and this with a large glass plate, which was turned round as soon as its lower surface became covered with drops of water, this treatment being repeated five or six times, without shaking the vessel.

*Potassium Ferrocyanide*,  $\text{K}^4\text{FeCy}^6 + 3\text{H}^2\text{O}$ , is usually regarded as belonging to the quadratic system (ii. 239). Wyruboff finds, however, that small, perfectly transparent crystals which separate from a solution of the salt mixed with neutral potassium chromate belong to the monoclinic system, having the axial ratio  $a : b : c = 0.401 : 1 : 0.395$ , and the angle  $ac$   $89.27^\circ$ . Under the microscope, these crystals appear optically biaxial; the apparent monoaxial character of the ordinary crystals of the salt is attributed by Wyruboff to the superposition of lamellae, in which the plane of the optic axis of one lamella is perpendicular to that of the next.

When potassium ferrocyanide is boiled with sal-ammoniac, the following reaction takes place (?):



The ferric cyanide,  $\text{Fe}^3\text{Cy}^6.3\text{H}^2\text{O}$ , is said to be precipitated as an extremely fine green powder, which does not alter when dried at  $100^\circ$ . The same green powder is said also to be frequently produced from the ferrocyanides of the earthy-alkali metals when they are exposed to the air, hydrocyanic being liberated at the same time. The crystals under these circumstances acquire a green colour and become yellow again, only after two recrystallisations.

A double salt of potassium ferrocyanide with the nitrates of potassium and sodium, having the composition  $\text{K}^4\text{FeCy}^6.2\text{NaNO}^3.2\text{KNO}^3$  or  $\text{K}^2\text{Na}^2\text{FeCy}^6.4\text{KNO}^3$ , is described by C. A. Martius (*J. pr. Chem.* xcvii. 502), as sometimes separating from the mother-liquors of saltpetre in the preparation of which waste potash-salts from the manufacture of yellow prussiate have been used; also as formed when a boiling solution of the nitrates of potassium and sodium is mixed with potassium ferrocyanide, and the mother-liquor which remains after the greater part of the potassium nitrate has crystallised out, is left to evaporate gradually. It is easily soluble in water, and separates therefrom in large, well-defined crystals of the hexagonal system, which exhibit the faces of several rhombohedrons in combination with the basal end-face ( $OR : R = 135^\circ 15'$ ) and acquire a tubular form from predominance of the end-face. The crystals are light yellow, hard, brittle, and yield a white powder. When exposed for some time to light, they become covered with a greenish coating, and when shaken or rubbed in the dark they shine with a faint, greenish light. They decrepitate when slightly heated, and detonate at a higher temperature, almost as strongly as gunpowder. Wyruboff did not succeed in preparing this double salt, and therefore assumes that it is a mere mixture.

*Sodium Ferrocyanide*,  $\text{Na}^4\text{FeCy}^6 + 12\text{H}^2\text{O}$ , which is less soluble than the potassium salt, may be prepared by double decomposition of the latter with any salt of sodium.

*Lithium Ferrocyanide*,  $\text{Li}^4\text{FeCy}^6 + 9\text{H}^2\text{O}$ , is extremely deliquescent, and therefore its amount of water is difficult to determine.

*Lithium-ammonium Ferrocyanide*,  $\text{Li}^2(\text{NH}^4)^2\text{FeCy}^6 + 3\text{H}^2\text{O}$ , is prepared by dissolving equivalent proportions of the ferrocyanides of lithium and ammonium in water, and leaving the solution, which is decomposed by heat, to evaporate in a vacuum. The crystals, which are never very well defined, are identical in form with those of the following salt.

**Lithium-potassium Ferrocyanide**,  $\text{Li}^2\text{K}^2\text{FeCy}^6 + 3\text{H}^2\text{O}$ , is prepared by treating commercial Prussian blue—which generally contains potassium ferrocyanide—with caustic lithia, concentrating the solution to a syrup, and then leaving it to evaporate over oil of vitriol. The mother-liquors, which contain pure lithium salt, yield a further quantity of the double salt on addition of potassium ferrocyanide. The salt dissolves in about  $1\frac{1}{2}$  part of water at ordinary temperatures, gives off 2 mols. water at  $100^\circ$ , and the rest at  $250^\circ$ , when also it begins to decompose. The crystals are monoclinic. Axes  $a : b : c = 1.353 : 1 : 1.516$ . Angle  $bc = 56^\circ 18'$ .

**Rubidium Ferrocyanide**,  $\text{Rb}^4\text{FeCy}^6 + 2\text{H}^2\text{O}$ , is isomorphous with the following salt, and dissolves at ordinary temperatures in less than its own weight of water.

**Thallium Ferrocyanide**,  $\text{Tl}^4\text{FeCy}^6 + 2\text{H}^2\text{O}$ , may be prepared by double decomposition, and obtained by slow cooling, in small highly lustrous crystals of the triclinic system, having the axes  $a : b : c = 1.2562 : 1 : 1.0547$ ; and the axial angles  $bc = 89^\circ 23'$ ;  $ac = 80^\circ 21'$ ;  $ab = 76^\circ 20'$ .

**Barium Ferrocyanide**,  $\text{Ba}^2\text{FeCy}^6 + 6\text{H}^2\text{O}$ , prepared by double decomposition with potassium ferrocyanide, and a large excess of a barium salt, requires for solution about 1,000 parts water at  $15^\circ$ , and 100 parts at  $75^\circ$ . Crystals monoclinic :  $a : b : c = 1 : 1.0017 : 0.9536$ . Angle  $bc = 72^\circ 48'$ .

**Barium-potassium Ferrocyanide**,  $\text{BaK}^2\text{FeCy}^6 + 5\text{H}^2\text{O}$ , which crystallises in the hexagonal system, is regarded by Wyruboff, as identical with the double salt prepared some years ago by Bunsen, although the latter found it to contain only 3 mols. water (ii. 221).

**Calcium Ferrocyanide**,  $\text{Ca}^2\text{FeCy}^6 + 12\text{H}^2\text{O}$ , prepared by saturating ferropicric acid with calcium carbonate, dissolves in 0.66 pt. water at  $90^\circ$ , and crystallises easily and well in a vacuum; nevertheless the crystals effloresce at  $25^\circ$ – $30^\circ$ , and give off  $11\frac{1}{2}$  mols. water at  $100^\circ$ , the rest only when they begin to decompose. Triclinic. Axial ratio,  $a : b : c = 1.2524 : 1 : 0.5435$ . Angle  $bc = 77^\circ 12'$ ;  $ac = 75^\circ 32'$ ;  $ab = 43^\circ 6'$ .

**Calcium-sodium Ferrocyanide**,  $\text{CaNa}^2\text{FeCy}^6$ , is difficult to prepare, and has been obtained only in small quantity. When a solution of the calcium and sodium salts in equivalent proportions is left to evaporate, it first deposits a large quantity of the sodium salt, after which a crust forms, made up of small, very regular quadrate crystals, consisting of the double salt contaminated with calcium ferrocyanide. The crystals are square prisms, approaching very closely to the cube, if they are not actual cubes. Their relation to polarised light, however, shows that they have a very complex structure, being made up of four, or even a larger number of separate crystals of various sizes.

**Strontium Ferrocyanide**,  $\text{Sr}^2\text{FeCy}^6 + 15\text{H}^2\text{O}$ , prepared like the calcium salt, is extremely soluble in water, and crystallises from a hot solution cooled to  $8^\circ$  or  $10^\circ$  in very fine monoclinic crystals, having the axes  $a : b : c = 1.645 : 1 : 1.061$ , and the angle  $bc = 58^\circ 24'$ . By dissolving this salt in water containing lithium ferrocyanide, and leaving the solution to evaporate in a vacuum over oil of vitriol, a 8-hydrated salt,  $\text{Sr}^2\text{FeCy}^6 + 8\text{H}^2\text{O}$  is obtained in triclinic crystals, having the axes  $a : b : c = 0.6753 : 1 : 0.2529$ ; and the angles  $bc = 84^\circ 42'$ ;  $ac = 88^\circ 34'$ ;  $ab = 63^\circ 38'$ .

**Strontium-potassium Ferrocyanide**,  $\text{Sr}^2\text{K}^2\text{FeCy}^6 + 3\text{H}^2\text{O}$ , may be prepared like the lithio-potassic salt; but the solution must be left to evaporate spontaneously, as when heated, it deposits the anhydrous double salt in the form of a white powder. The hydrated salt is slightly soluble in alcohol, begins to give off water at  $100^\circ$ , loses  $1\frac{1}{2}$  mol. at  $110^\circ$ , and the rest when it begins to decompose. The crystals, which are not very distinct, are monoclinic. Axes  $a : b : c = 0.64487 : 1 : 0.8944$ , Angle  $bc = 37^\circ 12'$ .

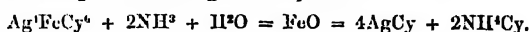
**Strontium-calcium Ferrocyanide**,  $\text{SrCaFeCy}^6 + 10\text{H}^2\text{O}$ , is prepared by direct union of the constituent salts. The solution, evaporated in a vacuum, yields large crystals which give off part of their water at ordinary temperatures and the whole at  $80^\circ$ . It dissolves very easily in about a third of its weight of water. Triclinic.  $a : b : c = 0.3534 : 1 : 0.3423$ . Angle  $bc = 89^\circ 18'$ ;  $ac = 77^\circ 9'$ ;  $ab = 82^\circ 34'$ .

**Cobalt Ferrocyanide**. An ammoniacal solution of cobalt nitrate forms with potassium ferrocyanide a precipitate of a fine green colour, which, on addition of a large excess of ammonia, is converted into a rose-red crystalline powder,  $\text{Co}^2\text{FeCy}^6 \cdot 12\text{NH}^3 + 9\text{H}^2\text{O}$ , which gradually changes to a brown mass, almost wholly soluble in acids, and when treated with a large quantity of water, is immediately converted into a dark green substance having the composition  $\text{Co}^2\text{FeCy}^6 \cdot 8\text{NH}^3 + 10\text{H}^2\text{O}$  (F. Curda, *Wien. Akad. Ber.* lviii. [2], 149).

**Copper Ferrocyanide**. According to Reindel (*J. pr. Chem.* ciii. 166), the so-

called 'Hatchett's Brown' produced by the reaction of potassium ferrocyanide with cupric salts, is not  $\text{Cu}^2\text{FeCy}^6$ , as generally supposed, but a double ferrocyanide,  $\text{Cu}^2\text{K}^2\text{FeCy}^{12}$ , even when formed in a solution containing excess of copper salt; when dried in the air, it has the composition  $\text{Cu}^2\text{K}^2\text{FeCy}^{12} + 12\text{H}^2\text{O}$ . In drying, its temperature should not exceed  $110^\circ$ , as decomposition takes place between  $130^\circ$  and  $140^\circ$ . Wyruboff on the other hand (*Bull. Soc. Chim.* [2], xii. 98; xiv. 145) denies that the precipitate contains potassium, unless a very large excess of potassium ferrocyanide is used in the precipitation. In all other cases it has the composition  $\text{Cu}^2\text{FeCy}^6$ , probably with 6 mols.  $\text{H}^2\text{O}$ . With regard to this controversy, it is remarked in the *Jahresbericht für Chemie*, 1869, p. 321, that a very important point appears to have been overlooked, viz. as to whether the solution of potassium ferrocyanide was gradually added to the copper solution or the copper solution to the ferrocyanide: in the latter case the precipitate always contains potassium, whereas in the former it may be free from that element.

**Silver Ferrocyanide**,  $\text{Ag}^4\text{FeCy}^6$ . According to Weith (*Zeitschr. f. Chem.* [2], v. 381), this salt is but slightly acted on by mercuric oxide; neither is it completely decomposed by potash. When, however, it is boiled with aqueous ammonia, complete decomposition takes place, according to the equation:



As the insolubility of silver ferrocyanide in ammonia is usually regarded as decidedly characteristic of that salt, ignorance of the reaction just noticed may easily lead to errors in qualitative analysis, especially when warm solutions are used, or even when the precipitated ferrocyanide is merely left for a short time in contact with the ammoniacal liquid.

When silver ferrocyanide is brought in contact with an ammoniacal solution of silver nitrate, ferric oxide is separated, and the whole of the silver is dissolved as cyanide; the same reaction takes place with ferrocyanide or ferricyanide of potassium, Prussian blue, &c.; even potassium cobalticyanide, which resists the action of mercuric oxide, is acted upon in the same way, if the temperature of the liquid be raised to  $150^\circ$ . The reaction is definite enough to be used for the quantitative estimation of cyanogen. For this purpose it is convenient to use sealed tubes heated for about four hours in the water-bath (Weith).

**Ammonio-ferricyanide of Silver**,  $\text{Ag}^4\text{FeCy}^6 \cdot 2\text{NH}^3$ , is precipitated as a white, heavy, distinctly crystalline powder, when potassium ferrocyanide is added to a solution of silver nitrate containing an excess of ammonia. It is also formed by the action of ammonia on moist silver ferrocyanide, and when ammonio-ferricyanide of silver  $\text{Ag}^4\text{FeCy}^{12} \cdot 3\text{NH}^3$  (1st Suppl. 534) is digested for some time, or warmed, with a large excess of ammonia, nitrogen gas being at the same time evolved. When dried over quick lime, it has the composition  $\text{Ag}^4\text{FeCy}^6 \cdot 2\text{NH}^3 + 6\text{H}^2\text{O}$ . It smells slightly of ammonia, retains its white colour unaltered at  $100^\circ$  or a little above, but at higher temperatures turns brown, and ultimately glimmers, giving off nitrogen and ammonium cyanide, and leaving a loose black mixture of paracyanogen, iron carbide, and silver carbide. It is nearly insoluble in boiling water, and very sparingly dissolved even by a large excess of ammonia (Genth *J. pr. Chem.* cviii. 109). The formation of the ammonio-ferricyanide of silver is contradictory to Wittstein's statement (*Gmelin's Handbook*, viii. 32), that silver ferrocyanide dissolves in ammonia, forming an opalescent liquid. Compare also Weith, (*supra*).

**Ferricyanides.** **Lead Ferricyanide**, formed by precipitation, is, according to Genth (*Wien. Akad. Ber.* lix. [2] 800), not anhydrous, as stated by Gmelin (*Handbook*, vii. 401), but hydrated, having the composition  $\text{Pb}^2\text{FeCy}^{12} + 10\text{H}^2\text{O}$ , and gives off its water at  $110^\circ$ . When prepared from sugar of lead containing lime, the crystals, without essential alteration of form, retain about 1 p.c. calcium. According to measurements by v. Zepharovich, they are monoclinic, having the axes  $a : b : c = 0.6558 : 1 : 1.0680$ , and the angle  $b c = 71^\circ 32' 33''$ .

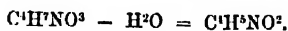
**Potassium Ferricyanide.**—Solutions of this salt are well known to decompose readily, with formation of ferrocyanide and a blue precipitate. The presence of organic matter facilitates this decomposition considerably, but light seems to be the chief cause. A solution of 1 part freshly prepared potassium ferricyanide in 10 parts of water, when exposed to diffused daylight, becomes darker in colour in the course of a few hours, while, if it is exposed to direct sunlight, the production of ferrocyanide may be demonstrated by means of ferric chloride, even after the lapse of only thirty seconds. Yellow light is without action on the solution, and no alteration was observed to take place in the solid salt. The action may be made use of for the production of photographic pictures, but this, owing to the unstable character of cyanogen-compounds, is not likely to be of any practical importance at present. Manufacturers may, however, find it advantageous to evaporate and crystallise solutions of red prus-

state in the dark, or by lamp-light, and test-solutions of ferricyanide should be kept in bottles of yellow glass (H. Vogel, *Deut. Chem. Ges. Ber.* iv. 90).

On the use of potassium ferricyanide as a test for cobalt, nickel, and manganese, see COBALT (p. 362).

**CYANITE.** A mineral called 'Glance-spar,' having the composition of cyanite  $Al^{IV}_2O_3 \cdot SiO_2$ , but differing from it in specific gravity and crystalline form, is found at several localities in the Siobengebirge (see GLANCE-SPAR).

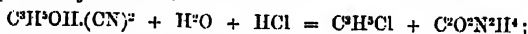
**CYANOCARBONIC ETHERS.** *Ethyl Cyanocarbonate*,  $C^2H^2NO^2 = CO \begin{Bmatrix} CN \\ OC^2H^2 \end{Bmatrix}$ , is formed by distilling a mixture of 3 parts phosphoric anhydride with 2 parts oxamethane :



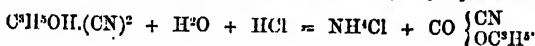
It is a colourless mobile liquid of ethereal, but penetrating odour, boiling at  $115^\circ$ – $116^\circ$ ; almost insoluble in water, but slowly decomposed thereby, with formation of alcohol, carbonic anhydride, and hydrocyanic acid. With alcoholic ammonia it forms a white product which appears to be the amide of cyanocarbonic acid (Weddige, *J. pr. Chem.* [2], vi. 117).

*Allyl Cyanocarbonate*,  $C^3H^2NO^2 = CO \begin{Bmatrix} CN \\ OC^2H^2 \end{Bmatrix}$ , is formed, simultaneously with oxamide, by the action of fuming hydrochloric acid on the dicyanide of allyl alcohol. The liquid becomes warm, and on the completion of the reaction, the temperature being kept down, a product is formed from which ammonium chloride and oxamide are deposited in the crystalline form; and on fractional distillation, allyl chloride and allyl cyanocarbonate are obtained.

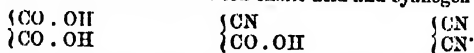
The reactions by which these bodies are formed seem to go on simultaneously. In the one cyanogen is detached from the allyl alcohol and converted into oxamide, while the alcohol yields allyl chloride :



in the other, ammonia only is removed, and the carbon of one of the cyanogen groups becomes linked, by means of oxygen, to the allyl, forming allyl cyanocarbonate :



Cyanocarbonic acid is intermediate between oxalic acid and cyanogen :



The formation of ethyl cyanocarbonate from oxamethane shows its relation to the former; that of allyl cyanocarbonate from allyl alcohol dicyanide, its relation to the latter (Wagner a. Tollens, *Deut. Chem. Ges. Ber.* v. 1045).

**CYANOFORM**,  $CH(CN)^3$ . According to T. Fairley (*Chem. Soc. J.* [2], ii. 362), this compound is formed by heating chloroform with potassium cyanide and a little alcohol to  $100^\circ$  in sealed tubes, as a non-volatile mass, pasty at ordinary temperatures and assuming the consistence of a viscid liquid at  $100^\circ$ . By the reducing action of tin and hydrochloric acid it is converted into a base,  $C^2H^2N^3$  or  $N^4(C^2H^2)^{III}H^2$ , called by Fairley tetrylin-triamine. This base boils above  $150^\circ$  and forms a platinum salt,  $2(C^2H^2N^3.3HCl).3PtCl^4$ .

According to Pfankuch (*J. pr. Chem.* [2], iv. 387; vi. 97), Fairley's method yields only traces of cyanoform, the main product consisting of a brown tarry mass. Small quantities of cyanoform are also formed by heating chloroform with silver cyanide. By carefully regulating the temperature ( $120^\circ$ – $130^\circ$ ), and the amount of alcohol added to the mixture of chloroform and potassium cyanide, a certain quantity of pure cyanoform may be obtained; it crystallises from an alcoholic solution on slow evaporation in small, yellowish-white needles, having a somewhat unpleasant odour. Cyanoform could not be obtained by heating iodoform with either mercury or silver cyanide, but by digesting with mercury cyanide and alcohol for some hours in sealed tubes at  $120^\circ$ , the whole was converted into a double compound of the formula  $2CH(CN)^3.3HgI^2$ . By treatment with ammonium sulphide this compound is converted into the corresponding ammonium double salt  $CH(CN)^3.3NH^2I$ , which crystallises in small deliquescent cubes. The greater part of the mercuric iodide may be removed from the mercuric double salt by treatment with water; but it has not yet been found possible to obtain pure cyanoform by this method. Cyanoform heated with soda or with aqueous hydrochloric acid is easily converted into methintricarmonic acid,  $CH(COOH)^3$ , which crystallises in small needles.

**CYANOGEN.** *Physical States.*—To liquefy cyanogen, a pressure of 4 atmospheres

is required at  $20^{\circ}$  and of  $1\frac{1}{2}$  atmosphere at  $0^{\circ}$ . Cyanogen is liquid under the ordinary pressure, at  $-21^{\circ}$  and solidifies at the freezing point of mercury (Hofmann, *Deut. Chem. Ges. Ber.* iii. 658).

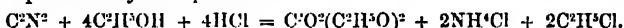
The solvent power of liquid cyanogen has been tested by G. Gore (*Proc. Roy. Soc.* xx. 67) as follows:—Highly dried mercuric cyanide in coarse powder was heated in a stout glass tube furnished with a V-shaped bend, and closed by a gutta-serena plug tied down with copper wire, the whole being protected by screens. The liquid cyanogen condensed in the bend, which was kept cool by a wet rag, the body to be tested for solubility having been previously placed in it.

*Substances soluble at  $15^{\circ}$ .*—Camphor, chloral hydrate, iodine, picric acid, and the disulphide, monochloride, dichloride, and trichloride of carbon. White phosphorus, cane-sugar, carbon tetrachloride, and water were only slightly soluble.

*Substances insoluble at  $15^{\circ}$ .*—Carbon, boron, silicon, sulphur, selenium, zinc, mercury, copper, iron, magnesium, salts, gums, fats, and most inorganic and organic substances.

Iodic acid became pink, cuprous iodide vermilion-red, ammonium carbonate brown. Moisture and alkalis caused the formation of a brown solid body, probably pure cyanogen.

*Decomposition of Cyanogen by Hydrochloric acid in presence of Alcohol.*—When cyanogen gas is passed into a saturated solution of hydrochloric acid in absolute alcohol, heat is evolved and a white crystalline precipitate forms in quantity proportional to the cyanogen employed. Under these conditions the precipitate consists of pure ammonium chloride; but if the solution be not saturated with hydrochloric acid, more or less oxamide is produced, and the mother-liquor contains oxalic ether together with a small quantity of formic ether, which may be detected by pouring the mother-liquor into dilute aqueous ammonia, separating the oxamide, acidifying the filtrate with sulphuric acid, distilling, saturating the distillate with calcium chloride, saponifying the ether which separates, and finally distilling with sulphuric acid. The distillate thus obtained exhibits the reactions of formic acid. The formation of oxalic ether is represented by the equation:



The formic ether results from the decomposition of part of the oxalic ether.

The reaction of cyanogen with hydrochloric acid in presence of alcohol, is different from that which takes place in presence of water, the cyanogen in the latter case being converted into oxamide, while the hydrochloric acid undergoes no change (*1st Suppl.* 538).

*Action of Ammonia on Cyanogen.*—Dry ammonia and cyanogen gas combine forming hydrazulmin,  $\text{C}^2\text{N}^2\text{H}^2$ , in amorphous, jet-black scales, which, when heated, first decrepitate violently, then swell up like Brodie's graphitic acid, giving out gases, and leaving a residue of paracyanogen, which volatilises completely at a higher temperature.

Water acts on hydrazulmin, forming hydrazulmoxin,  $\text{C}^2\text{N}^2\text{H}^2\text{O}$ :



Hydrazulmoxin is a brown amorphous mass which dissolves but sparingly in water, more freely in presence of ammonia. When the ammoniacal solution is exposed to the air, the hydrazulmoxin separates out again gradually. This compound is identical with the so-called azulmic acid, which is formed by the spontaneous decomposition of an aqueous solution of cyanogen, and by the action of cyanogen on aqueous ammonia. The more concentrated the latter, the greater is the quantity of azulmic acid formed, whilst in more dilute solutions the formation of oxamide preponderates. A hot aqueous solution of azulmic acid exhibits a fine violet fluorescence; on heating it gently with caustic potash or concentrated sulphuric acid, yellowish-brown solutions are obtained, which, after cooling, show a dark green fluorescence.

When azulmic acid is boiled with water and the hot solution filtered, it separates out on cooling with a much lighter colour; and, by repeating this operation several times, a product is at length obtained, forming light yellow amorphous flakes. This body is identical with mycomelic acid,  $\text{C}^2\text{N}^2\text{H}^2\text{O}^2$ , which Liebig and Wöhler first obtained by the action of ammonia upon alloxan, and which Hlasiwetz afterwards prepared by heating uric acid and water together in sealed tubes to  $180^{\circ}$ . Mycomelic acid is formed according to the equation:



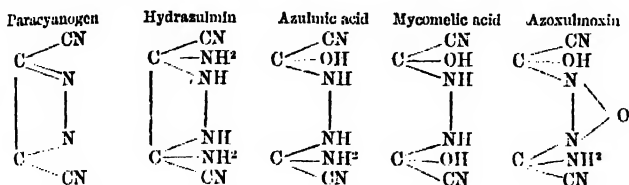
Mycomelic acid is soluble in boiling water; the solution shows a fine greenish-blue fluorescence.

By oxidising azulmic acid with potassium permanganate or nitric acid two atoms of hydrogen are replaced by oxygen and azoxulmoxin  $2\text{C}^2\text{N}^2\text{H}^2\text{O}^2 + \text{H}^2\text{O}$  is formed,



a reddish-yellow, crystalline powder, insoluble in water, but readily soluble in concentrated sulphuric acid. This solution shows an intense light green fluorescence, like uranium glass.

The constitution of these different compounds is most probably as follows:—



(Jacobson and Emmerling, *Deut. Chem. Ges. Ber.* v. 947).

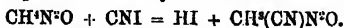
The name *azulmic acid* has also been given to an oxidised acid, which is one of the constituents of the reddish-black mass (azulmin) formed, after long standing, in hydrocyanic acid mixed with a little water and a trace of ammonia or a fixed alkali. According to Gautier (*Ann. Chim. Phys.* [4] xvii. 158) this mass consists of five different parts: (1.) A portion volatile at 100°, containing water, ammonia, and ammonium cyanide. (2.) A portion soluble, with red colour, in alcohol of 99 p.c., and crystallising therefrom in tufts. (3.) A portion soluble in somewhat dilute potash-ley. The dark brown filtered solution mixed with hydrochloric acid, deposits light flocks, while one or more nitrogenous bodies remain dissolved. (4.) A brown-black, uncrystalline, non-hygroscopic mass, forming by far the largest proportion of the whole, insoluble in water either cold or warm, also in alcohol, dilute acids, and dilute potash-ley, very slightly soluble in glacial acetic acid. With strong potash-ley it forms a dark brown solution, from which it is precipitated by hydrochloric, sulphuric, and even carbonic acid. It dissolves at ordinary temperatures in commercial nitric acid, and in strong sulphuric acid, and is separated therefrom by a large quantity of water. Its solution in acids forms brown precipitates with silver nitrate and mercury salts, green with copper salts, white with lead salts. Neither of these precipitates is crystalline. The sulphuric acid solution undergoes alteration when heated above 200°. The mass itself is unalterable at 130° and probably at much higher temperatures. By prolonged boiling with water in which insoluble bases like magnesia and zinc-oxide are suspended, it may be made to unite with those bases and form salts. (5.) A small quantity of a pitchy substance insoluble in concentrated acids.

The brown-black substance (4.) (azulmic acid) has, according to Gautier, the empirical formula  $\text{C}^2\text{H}^2\text{N}^2\text{O}$ , but its silver salt has the composition  $\text{C}^2\text{H}^2\text{AgN}^2\text{O}^2$ , whence it is probable that the acid itself is  $\text{C}^2\text{H}^2\text{N}^2\text{O}^2$ . Gautier assigns to it the constitutional formula,  $\text{N} \begin{array}{c} \text{CO} \\ | \\ \text{H} \end{array} \cdot 2\text{CNH}$ , supposing it to contain a polymerised cyanide of hydrogen.

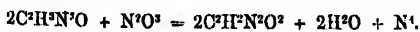
On the reaction of cyanogen chloride with phosphine, see PHOSPHINE; with *benzyl alcohol*, p. 178.

On the Heat of Formation of Cyanogen-compounds, see HEAT.

**CYANUREA**, or **CYANCARBAMIDE**,  $\text{C}^2\text{H}^2\text{N}^2\text{O} = \text{CH}^2(\text{CN})\text{N}^2\text{O}$ . Produced, according to Poensgen (*Ann. Ch. Pharm.* cxxviii. 339), by heating urea (30 parts) with cyanogen iodide (70 parts) for two days to 140°–150°:



On treating the product with warm water, and removing the separated iodine with sulphurous acid, cyanurea remains as an amorphous light yellow powder, nearly insoluble in water, easily soluble in strong acids and alkalis, not decomposed by acids even at the boiling heat, but resolved by heating with alkalis into ammonia and carbonic acid. Heated with barium hydrate and a little water to 130°, it yields, together with ammonia and barium carbonate, a barium salt containing  $(\text{C}^2\text{H}^2\text{N}^2\text{O})^2\text{Ba} + \text{H}^2\text{O}$ . Suspended in water and treated with nitrous acid, it is converted into dicyanic acid:



According to Hallwachs (*Zeitschr. f. Chem.* [2], vi. 354), Poensgen's cyanurea is nothing but impure ammeline  $\text{C}^2\text{H}^2\text{N}^2\text{O}^2$ , and his dicyanic acid is probably cyanuric acid.

**CYANURIC ACID AND ETHERS**, see pp. 406, 409.

**CYCLAMEN** (De Luca, *Gazzetta chimica italiana*, ii. 556). The tubers of

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*Cyclamen europæum* contain a fermentable saccharine substance, starch, and gum, together with acrid and poisonous matters, the most abundant of which is a non-nitrosated glucoside called cyclamin, which was prepared and described by De Luca about fifteen years ago (ii. 294). The paper above cited contains nothing new respecting this body, excepting a more expeditious mode of preparation, founded on its property of coagulating like albumin when its aqueous solution is heated. When the expressed juice of the tubers is heated nearly to the boiling point, a white flocculent substance separates on the surface, which may either be skimmed off, or separated by filtering the hot liquid. This substance dissolves in hot alcohol, and the solution filtered while still hot, deposits the cyclamin on cooling in the amorphous aggregations formerly described.

The juice of the tubers left to itself for some days in contact with the air, soon ferments, with evolution of carbon dioxide and formation of alcohol, which may be isolated by simple distillation. The cyclamin in the solution is at the same time coagulated by the heat developed by the fermentation. The filtered liquid evaporated to dryness over the water-bath leaves a brownish residue, the solution of which in cold alcohol yields by spontaneous evaporation, crystals of mannite. The mannite may also be extracted by treating the above-mentioned residue with hot alcohol, and leaving the solution to cool; it appears to be a product of the fermentation above mentioned: for the unfermented juice, treated in the manner just described, does not yield a trace of it. Further experiments must decide whether the mannite is formed by transformation of the cyclamin, or of the numerous other substances contained in the juice.

Other saccharine substances, more or less resembling mannite, have likewise been obtained from the juice of cyclamen. A considerable quantity of the juice having been boiled, the coagulum collected in filters, and these, after the liquid had drained off, having been placed under a bell-jar and surrounded with fragments of quick lime, renewed as it slaked, the whole of the coagulum was found, after some weeks, to be converted into a crystalline substance exhibiting some of the properties of mannite.—Another portion of the expressed juice poured into two glass vessels of 10 litres capacity, began, after a few days, to deposit, on the side more directly exposed to the light, a white, amorphous substance, which gradually increased in quantity; no gas was evolved, and the liquid did not exhibit any sign of putrefaction. On boiling the remaining liquid, only a small quantity of coagulum was obtained, and on separating the liquid therefrom, evaporating to dryness, and treating the blackish residue with hot alcohol, a solution was obtained which gradually deposited a crystalline substance likewise resembling mannite in some of its characters.

Lastly, the remaining portion of the juice was evaporated over the water-bath, the residue, when dry, was digested with cold alcohol, and the filtered liquid, while still hot, was left to itself in a glass vessel: it then deposited an amorphous substance, resembling the cyclamin which separates on cooling from an alcoholic solution.

These experiments seem to show that cyclamin is capable of gradually passing, under the influence of moisture, into a sweet crystallisable substance, similar to, or perhaps identical with, mannite.

The juice of cyclamen tubers may be introduced into the stomach of rabbits in doses of 10 to 20 grams without destroying life, and the tubers are eaten with impunity by pigs, but the juice, mixed with water in the proportion of 1 cub. cent. to 2 or 3 litres acts poisonously on fishes. The toxic action of cyclamin is similar to that of curarine, but less energetic, and, like the latter, it is nearly neutralised by bromine.

**CYCLOPIC ACID.** An acid obtained from *Cyclopia Vogelii*, a plant used in Africa for the preparation of tea. When about a pound of the dry leaves is tied up in a cloth, immersed in water for some days, and pressed from time to time, the cyclopic acid is deposited in the form of a yellow powder. It may be purified by crystallisation from weak spirit. It exhibits a deep greenish-yellow fluorescence, which is best observed when a few crystals of the substance are immersed in soda-ley, and exposed to sunshine: after a few days, however, the fluorescence disappears. Analysis leads to the formula  $C^7H^6O^4$  or  $C^4H^4O^3$ , the acid being bibasic or quadribasic accordingly (Church, *Chemical News*, xxii. 2).

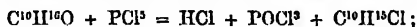
**CYMENE**,  $C^{10}H^{14}$ . The researches of Fittig, Kübrich a. Jilke, of Pott, of Louguine, and quite recently those of Boilstein a. Kupffer (*Deut. Chem. Ges. Ber.* vi. 1181; *Ann. Ch. Pharm.* clxx. 282), have shown that the cymene obtained from cuminal oil, and from the oil of *Cicuta virosa* is identical with that which is produced by dehydration of camphor with zinc chloride, phosphoric oxide, or phosphoric sulphide. The cymene obtained from these sources boils at  $175^\circ$ , has a specific gravity of 0.871–0.873 at  $0^\circ$ , and is converted by oxidation with dilute nitric acid into toluic acid, by oxidation with chromic acid mixture into acetic and terephthalic acids: hence it is

inferred to have the constitution of methyl-propyl-benzene, or methyl-isopropyl-benzene,  $C^6H^3(CH^3)(C^3H^7)$  (1st Suppl. 302).

The same cymene is produced by dehydrogenation of various hydrocarbons of the terpene group,  $C^{10}H^{16}$ , which, in fact, may be regarded as dihydrides of cymene. By adding bromine to oil of turpentine or oil of lemons at a low temperature, or by heating finely powdered turpin to  $50^\circ$ , and then leaving it to itself at the ordinary temperature, terpene dibromide,  $C^{10}H^{16}Br^2$ , is formed as a heavy oil, which, when heated with aniline to  $180^\circ$  for eight hours, gives up  $2HBr$  and yields cymene boiling at  $176^\circ$ – $179^\circ$ , and converted by oxidation with chromic acid into acetic and terephthalic acids (Oppenheim, *Deut. Chem. Ges. Ber.* v. 34, 628). A similar result has been obtained by Barbier (*Comptes rendus*, lxxiv. 194), by treating crystallised turpin  $C^{10}H^{16}$ ,  $3H^2O$  with bromine, and decomposing the product by distillation.

Wright (*Chem. Soc. J.* [2], xi. 686) has examined the cymenes obtained from various members of the terpene family by the following processes:

1. By acting on myristical (the chief constituent of volatile oil of nutmeg) with phosphorus pentachloride, whereby a liquid chloride  $C^{10}H^{16}Cl$  is obtained:



and this when heated to  $170^\circ$ – $190^\circ$ , is resolved into hydrogen chloride and cymene.

2. By the action of zinc chloride on myristical:  $C^{10}H^{16}O - H^2O = C^{10}H^{14}$ .

3. By digesting the chlorinated product obtained by the action of phosphorus pentachloride on cumphor, in a flask with vertical condenser, as long as hydrogen chloride was given off, then distilling off the remaining hydrocarbon, and digesting it with sodium. A polymoride of cymene appears to be formed at the same time in small quantity, and a viscid tar remains in the retort.

4. By treating the most volatile hydrocarbon of nutmeg oil (boiling at  $163^\circ$ – $164^\circ$ ) with sulphuric acid, the terpenes present are polymerised, and cymene pre-existing in it, remains unaltered: the cymene may then be distilled off.

5. Turpentine oil, treated in the same manner, likewise yields about 3 p.c. of cymene previously contained in it.

6. By adding bromine to hesperidene (from oil of orange-peel) and heating the resulting dibromide:  $C^{10}H^{16}Br^2 = 2HBr + C^{10}H^{14}$ .

7. From cumin oil, by the usual process of separating the cuminic aldehyde by combination with acid sodium sulphite, and distilling off the cymene.

The cymenes from these several sources all gave by analysis numbers agreeing with the formula  $C^{10}H^{14}$ , and their boiling points (corrected) though varying one or two degrees, were all about  $176^\circ$ . By oxidation with chromic acid mixture, they all yielded terephthalic and acetic acid, but no isophthalic acid, nor any of the higher homologues of acetic acid. Moreover, these seven samples had all the same odour, and their specific gravity, refractive index, and dispersion were nearly the same, approximating to the following mean values:

Sp. gr.	Refr. Index.	Dispersion.
0.86	1.48	0.035.

The optical properties of these cymenes have been examined by Gladstone (*Chem. Soc. J.* [2], xi. 970), who finds that they are practically the same for all, the specific refractive energy being 0.55, and their mean refraction-equivalent 75.1, the difference of the extremes not being greater than that usually observed between different specimens of the same hydrocarbon. This equivalent, calculated with the common refraction-equivalents for carbon (5) and for hydrogen (1.13), would give 68.2; thus all these specimens of cymene showed a higher equivalent characteristic of the aromatic group. This is particularly remarkable, as some of them were prepared from substances which do not exhibit this abnormal influence on light, affording additional evidence that the retarding power of the carbon in such bodies as these does not arise from any particular internal structure capable of being transmitted from one compound to another.

The boiling points and the specific gravities at different temperatures of the cymenes from several sources, carefully purified by treatment with sodium and subsequent fractional distillation have recently been determined with great care by Pisati & Paternò (*Gazzetta chimica italiana*, iii. 551), the result being to establish their identity with regard to these properties.

	From Cumin Oil.	From Cymyl Alcohol.	From Camphor.	From Thyme Oil.
Boiling point (bar. at 761·4 -761·6 mm.)	175·1°	177·25°	176·55°	
Sp. gr. at 0°	0·87446	0·87227	0·87221	0·87226
25°	0·85457	0·85258	0·85237	0·85244
50°	0·83459	0·82352	0·83251	0·83252
75°	0·81409	0·81209	0·81230	0·81223
100°	0·79307	0·79129	0·79123	0·79124

**Bromocymene**,  $C^{10}H^{13}Br = C^6H^5Br.CH^3.C^4H^7$ , is formed by adding bromine, drop by drop to cymene (prepared by the action of phosphorus pentasulphide on camphor). When purified by distillation with water and fractional distillation, it forms a liquid having a faint odour like that of cymene, boiling at  $233^{\circ}$ – $235^{\circ}$ , and having a sp. gr. of 1·269 at  $17\cdot5^{\circ}$ . The bromine in this compound is retained with great force, not being eliminated by the action of sodium and methyl iodide, or of sodium and carbon dioxide.

Bromocymene is readily oxidised by dilute nitric acid (1 acid to 4 water) forming bromotoluic acid,  $C^6H^5Br.C^4H^7(COOH)$ , melting at  $203^{\circ}$ – $204^{\circ}$  (Landolph, *Deut. Chem. Ges. Ber.* v. 267). See TOLUIC ACIDS.

**Chlorocymene** is formed when chlorine gas, diluted with carbon dioxide, is passed into cymene. Heated with potassium acetate and alcohol, it yields cymyl acetate,  $C^{10}H^{13}.C^2H^3O^2$ , a liquid boiling above  $236^{\circ}$  (Czumpelik, *Deut. Chem. Ges. Ber.* iii. 481).

**CYMESE-SULPHONIC ACID**,  $C^{10}H^{13}.SO^2H$ , is mentioned in the *First Supplement* (p. 302), as formed by treating cymene with fuming sulphuric acid. According to H. Müller (*Deut. Chem. Ges. Ber.* ii. 130), it is also very easily produced by treating pure cymene with ordinary sulphuric acid at  $90^{\circ}$ – $100^{\circ}$ . Heated with caustic potash or soda it yields oxycymene or cymic phenol,  $C^{10}H^{14}OH$ .

Beilstein u. Kupffer (*Deut. Chem. Ges. Ber.* vi. 1181; *Ann. Ch. Pharm.* clxx. 287) have examined several salts of the cymene-sulphonic acids prepared from cymene obtained from cumin oil and from camphor, and have found them to be identical in their properties. The *barium salts*,  $(C^{10}H^{13}SO^2)^2Ba + 3H^2O$ ,\* form crystalline laminae, which do not give up their water of crystallisation till heated above  $100^{\circ}$ . 100 parts of water at  $16\cdot2^{\circ}$  dissolve 2·5 parts of the hydrated salt; 100 parts of alcohol at  $17\cdot5^{\circ}$  dissolve 5·3–5·5 parts. The *calcium salt*,  $(C^{10}H^{13}SO^2)^2Ca + 2H^2O$ , crystallises by slow cooling from a not too concentrated solution in splendid large plates which have a vitreous lustre, give off their water of crystallisation over sulphuric acid, and are much more soluble in water than the barium salt. The crystals are monoclinic, exhibiting the combination  $\infty P_{\infty} . + P . - P . \infty P . \infty P_3$ . Ratio of axes  $a : b : c = 1\cdot373958 : 1 : 1\cdot124195$ . Angle  $bc = 95^{\circ} 13' 17''$ . Cleavage very distinct parallel to  $\infty P_{\infty}$  and  $(\infty P_{\infty})$  (Jerosfjew, *Ann. Ch. Pharm.* clxx. 297).

The *lead-salt*,  $(C^{10}H^{13}SO^2)^2Pb + 3H^2O$ , forms shining laminae which give off their water over oil of vitriol. 100 parts water at  $16^{\circ}$  dissolve 1·34–1·94 parts of the salt. The solution is partially decomposed by evaporation.

According to Paternò (*Gazzetta chimica italiana*, iii. 544), cymene from camphor yields two isomeric sulpho-acids, the barium salt of one of which contains  $3H^2O$ , while that of the other contains only  $1H^2O$ . This may perhaps account for the earlier statements respecting this salt (ii. 299), according to which it crystallises sometimes with 2, sometimes with only 1 mol. water.

**CYMIC PHENOL or OXYCYMENE**,  $C^{10}H^{14}O = C^{10}H^{13}OH$ , is produced by the action of caustic alkalis on cymene-sulphonic acid (*vid. sup.*, also *1st Suppl.* 302), also, together with camphor, camphoretin and colophene, by the action of iodine on camphor (Claus, *J. pr. Chem.* xxvi. 261; Schweizer, *ibid.* 118). According to Fleischer u. Kekulé (*Deut. Chem. Ges. Ber.* vi. 934), the best mode of preparing it from camphor is the following:

Camphor is heated with about one-fifth of its weight of iodine in a vessel connected with a reversed condenser, and the product submitted to distillation, until the tempe-

\* In the *First Supplement* (p. 302) this salt is erroneously stated to contain 6 mol. water.

nature of the vapour is  $170^{\circ}$ . The residue is treated with concentrated soda-ley, which leaves a resinous body undissolved, and the filtrate is shaken repeatedly with ether; on adding hydrochloric acid to the filtrate, the phenol separates out. It is an oily liquid, which does not solidify at  $-20^{\circ}$ , and boils at  $231^{\circ}$ – $232^{\circ}$ . By the action of phosphorus pentasulphide, it is converted into cymene, and a thiocymene or cymic mercaptan, which is identical with that obtained by distilling camphor with phosphorus pentasulphide. These results show that in cymene-sulphonic acid, and in the phenol and mercaptan derived from it, the inorganic groups occupy the same position as in the cymic phenol and mercaptan derived from camphor (Raderburg, *Deut. Chem. Ges. Ber.* vi. 669).

**CYMIC MERCAPTAN** or **CYMENYL SULPHYDRATE**,  $C^{10}H^{13}SH$ , is formed in small quantity, together with other compounds soluble in alkalis, in the preparation of cymene by distilling camphor with phosphoric sulphide (1st Suppl. 302). To free these soluble compounds from hydrocarbons, the alkaline solution is either shaken with ether, or subjected to the action of a current of steam; afterwards the solution is acidified with hydrochloric acid, and the oil which separates is subjected to fractional distillation. The principal product thus obtained is cymene-mercaptan (Flesch). It is also produced by distilling cymic phenol with phosphorus pentasulphide, and by the action of nascent hydrogen on cymene-sulphonic chloride,  $C^{10}H^{13}SO_2Cl$ , obtained by distilling the potassium salt of cymene-sulphonic acid with phosphorus pentachloride (Raderburg, *Deut. Chem. Ges. Ber.* vi. 669).

Cymic mercaptan is a colourless liquid, having a peculiar aromatic odour, miscible with alcohol, but insoluble in water. It has a sp. gr. of 0.9975, and boils at  $235^{\circ}$ – $236^{\circ}$ . Oxidising agents transform it into cymene disulphide.

The *mercury compound*  $Hg(C^{10}H^{13})_2SS^2$ , is obtained in long, bright needles, by boiling an alcoholic solution of the mercaptan with mercuric oxide, and cooling the liquid, or as a white precipitate by mixing an excess of an alcoholic solution of the mercaptan with mercuric chloride. On distillation, it yields metallic mercury, mercuric sulphide, and an oil which appears to be a mixture of monosulphide and disulphide of cymene. When an alcoholic solution of cymic mercaptan is added to excess of mercuric chloride, a more soluble compound,  $C^{10}H^{13}S.HgCl$  is formed. The *silver-compound*  $C^{10}H^{13}AgS$  is obtained as a yellow-crystalline precipitate on adding an excess of solution of the mercaptan to a solution of silver nitrate. If the mercaptan is not in excess, the compound  $C^{10}H^{13}Ag_2S.AgNO_3$  is formed, which crystallises from alcohol in leaflets (Flesch, *Deut. Chem. Ges. Ber.* vi. 478).

*Cymic Disulphide*,  $(C^{10}H^{13})_2SS^2$ , is formed by oxidation of cymic mercaptan, and is best prepared by dissolving the latter in an alkali, and adding sodium. It then separates as an oil, which does not solidify on refrigeration (Flesch).

When cymic mercaptan or cymic disulphide is treated with nitric acid, two atoms of carbon are eliminated, and sulphotoluic acid,  $C^8H^5 \begin{Bmatrix} SO^2H \\ CO^2H \end{Bmatrix}$ , is formed (Flesch).

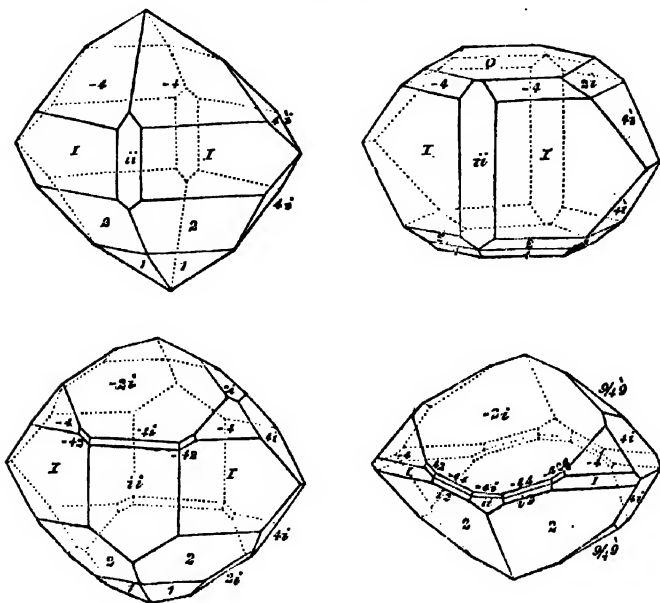
## D.

**DAMBONITE**,  $C^4H^5O^3$ . This saccharine substance, obtained from the West Coast of Africa (1st Suppl. 541), is converted, by a mixture of nitric and sulphuric acids, into a thick, translucent, gummy nitro-compound, which is precipitated in flakes by water, crystallises from solution in boiling alcohol, and detonates when struck (Champion, *Compt. rend.* lxxiii. 114).

**DAPHNE**. The seeds of *Daphne Mezereum* yield a fat oil, which has a specific gravity of 0.8903 at  $15^{\circ}$ , dissolves slightly in alcohol, remains fluid at  $16^{\circ}$ , and dries up on wood. It contains an acid substance, from which it may be freed by digestion with alcohol. By saponification, it yields stearic, palmitic, myristic and linoleic acids. The press-cake yields to ether a resin, and to alcohol of 95 p.c. a resinous substance, which, after treatment with alcohol of 70 p.c. crystallises from hot alcohol in stellate groups. This substance is coccognin (p. 386). 100 parts of mezereum fruit yielded, together with traces of volatile oil, 31 parts fat oil, 3.58 resin and wax soluble in ether, 0.32 acrid resin (soluble in alcohol), 0.38 coccognin, 19.5 protoids, 32.37 mucus, gum, plant-acids, bitter principles, colouring matter and cellulose, 5.46 inorganic matter, and 7.39 water (Casselmann, *Jahresb.* 1870, 883).

**DATOLITE.** This mineral occurs abundantly in brilliant crystals exhibiting a great variety of combinations, in the Bergen Hill Tunnel, New Jersey. An elaborate description of these crystals, accompanied by figures, is given by E. S. Dana (*Sill. Am. J.* [3], iv. 16), whose measurements show that they are monoclinic, differing but slightly from the orthorhombic form, a result agreeing with the measurements of Kopp (ii. 305). The crystals are referrible to four distinct types, which are represented in the following figures : \*

FIG. 12.



**DATURA.** The following method, devised by Dragondorff, for estimating the amount of alkaloid in *Datura Stramonium*, and *Atropa Belladonna*, is described by N. Günther (*Zeitschr. Anal. Chem.* viii. 4761). The comminuted plant-organs are twice exhausted at 30°-40°, with 10 times their weight of water acidulated with 3 drops of sulphuric acid, and the strained extracts are evaporated to a syrup over a steam-bath. The syrupy liquid is left for 24 hours in contact with three times its volume of alcohol, to separate gummy substances, then filtered; the greater part of the alcohol is removed by distillation, the rest by evaporation over a water-bath; and the residue is agitated with light petroleum oil to free it from colouring and resinous matters. The liquid is then neutralised with ammonia; the alkaloids are dissolved out by repeated treatment with chloroform; the united extracts are freed from ammonia salts by washing with water; and the residue left, after removing the greater part of the chloroform by distillation, and the rest by evaporation, is weighed. The roots, leaves, ripe and unripe fruit of *Belladonna* thus treated, yield the alkaloid as a colourless, spicular, crystalline mass; the stems yield it as an amorphous mass, whereas from all parts of the *Datura*, yellow amorphous daturine is obtained. The amorphous portions treated with water containing sulphuric acid, always leave a slight resinous residue. The weight-determinations may be verified by titration with potassium-mercuric iodide (1st Suppl. 86). The results are given on page 117 of this volume.

**DECANE**,  $C^{10}H^{22}$ , is the chief product obtained by heating turpentine oil to 275° for 24 hours with 60 parts of hydriodic acid. It boils between 155° and 162°, withstands the action of nitric acid, and is not attacked by bromine at ordinary temperatures. *Pentane* or *Amyl Hydride*,  $C^5H^{12}$ , is formed at the same time in smaller quantity (Berthelot, *Bull. Soc. Chim.* [2], xi. 3).

\* The notation of the faces in these figures is that used in Dana's *Mineralogy*, for an explanation of which, see the article *Crystallography*, ii. 145, footnote.

**DECENE**,  $C^{10}H^{20}$ , and **DECINE**,  $C^{10}H^{18}$ , are obtained (together with larger quantities of a volatile aromatic hydrocarbon) by heating turpentine oil for some hours to  $200^{\circ}$ – $250^{\circ}$  with 20 parts of hydriodic acid. *Decene* boils at  $165^{\circ}$ , has a strong alliaceous odour, is not attacked by ordinary sulphuric acid in the cold, but dissolves in the fuming acid when heated, forming a sulpho-acid. Fuming nitric acid in the cold converts it into a nitro-acid, without evolution of red fumes. Bromine converts it, with evolution of hydrobromic acid, into colourless crystalline needles. *Decine* boils at  $170^{\circ}$ – $175^{\circ}$ , withstands the action of sulphuric acid, nitric acid and bromine more obstinately than decene; nevertheless it is gradually oxidised by boiling with nitric acid, and converted into a viscid product by heating with fuming sulphuric acid. Heated to  $280^{\circ}$  with hydriodic acid, it is converted into decane, with evolution of a gaseous mixture of 57 parts hydrogen and 43 propane (Berthelot, *loc. cit.*).

**DECEMENTE.** See VANADATES OF LEAD.

**DEHYDRATION.** A theoretical paper on the dehydration of organic compounds, and the part which this process plays in the formation of sugar, and on fermentation, has been published by A. Baeyer (*Deut. Chem. Ges. Ber.* 1870, 63; *Chem. Centralblatt*, 1871, 27, 38; *Chem. Soc. J.* [2], ix. 331).

**DELESSITE.** A mineral allied to delessite occurs in cavities of the trapp in the western part of New Caledonia, sometimes filling these cavities alone, sometimes encrusting zeolites. It is green, soft, fusible at the edges, partly soluble in hydrochloric acid. Analysis gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO.	CaO.	MgO.	Gangue.	H <sub>2</sub> O.	O. and loss.
40.53	6.95	12.50	0.52	14.15	2.87	13.10	9.38 = 100.

The iron occurs partly as  $Fe^{+}O^{+}$  (H. How, *Phil. Mag.* [4], xxxvii. 269).

Another mineral allied to delessite, occurring, on the Puy de Montandoux, Auvergne, as a cement of basaltic tufas, and in cavities of the same, has been analysed by v. Lasaulx (*Jahresb.* 1870, 1306), with the following results:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>2+</sup> O <sup>+</sup>	CaO.	MgO.	H <sub>2</sub> O.
30.32	18.51	19.82	4.51	11.74	12.30. = 100.20

**DEOXYBENZOLIN.** See BENZOIN (p. 172).

**DEOXYCODEINE.** See CODEINE.

**DEOXYGLUTANIC ACID**,  $C^5H^7O^4$ . An acid produced by heating glutanic or glutaric acid,  $C^5H^7O^3$  (*1st. Suppl.* 637), with four times its weight of concentrated hydriodic acid to  $120^{\circ}$  for about eight hours. It is very readily soluble in water, alcohol, and ether, and crystallises exceedingly well, forming large, transparent, monoclinic crystals, melting at about  $97^{\circ}$ , and decomposing above  $280^{\circ}$  into water and the anhydride.

*Acid Ammonium deoxyglutamate*,  $C^5H^7(NH^4)O^4$ , remains, on evaporating a strongly ammoniacal solution of the acid under an exsiccator, in transparent concentrically grouped crystals. *Calcium deoxyglutamate*,  $C^5H^7CaO^4 + H^2O$ , is sparingly soluble in water, and forms opaque laminae. *Barium deoxyglutamate*,  $C^5H^7BaO^4 + 5H^2O$ , crystallises in small transparent needles, readily soluble in water. *Lead deoxyglutamate*,  $C^5H^7PbO^4$ , is a white heavy precipitate, and the silver salt,  $C^5H^7Ag^2O^4$ , a very bulky precipitate resembling alumina; it is but sparingly soluble in boiling water, and separates on cooling in the crystalline state. It may be obtained in distinct needles by boiling a dilute solution of the acid with silver carbonate; but the greater part of the salt remains behind with the excess of silver carbonate.

Deoxyglutanic acid is isomeric with pyrotartaric acid, from which it follows that glutanic acid is not identical with either of the three homomalic acids derived from acconitic acid, as these latter would yield pyrotartaric acid by reduction (Dittmar, *J. pr. Chem.* [2], v. 338).

**DESCLOIZITE.** See VANADATES OF LEAD.

**DESMIN.** See STILBENE.

**DETONATION.** See EXPLOSION.

**DEXTRIN.** According to Jacobson (*Ann. Ch. Pharm.* clvii. 227) this substance occurs, together with inosite, in the lungs of the porpoise.

According to Musculus (*Bull. Soc. Chim.* [2], xviii. 66) dextrin is formed by the dehydration of glucose. Proceeding on the view that dextrin is the ether of glucose, he prepared sulphoglucosic acid by dissolving dry glucose in concentrated sulphuric acid, mixed the solution with alcohol of  $95^{\circ}$ , in which dextrin is very nearly insoluble, and set the mixture aside. A deposit, apparently dextrin, continued to form for about three weeks. Freed from adhering acid and alcohol, this deposit possessed the follow-

ing properties:—It was gummy while moist; amorphous and friable when dry; was very soluble in water, insoluble in alcohol; had no sweet taste; did not reduce copper salts; was only very slightly saccharified by diastase; was slowly converted into glucose by boiling with dilute sulphuric acid; and was not coloured by iodine. Its rotatory power, however, although very nearly double that of glucose, was still far below that of ordinary dextrin.

Respecting the formation of dextrin from starch, and the behaviour of dextrin and starch with iodine, see STARCH.

**DEXTRONIC ACID**,  $C^6H^{12}O_7$  (Habermann, *Deut. Chem. Ges. Ber.* v. 167). This acid, which has the same composition as gluconic acid, is obtained from dextrin in the same way as lactic acid from milk-sugar, *i.e.*, by bromination and treatment with silver oxide. The crude acid yields a crystallisable calcium salt, and is best purified by precipitating with lead acetate and treatment with sulphuretted hydrogen; it then forms a sour uncrystallisable syrup. Its ordinary salts are monobasic, but bibasic salts may be prepared in the same way as the corresponding salts of gluconic acid (*q.v.*), with which it is merely isomeric and not identical. The two acids differ by  $5^\circ$  in their molecular rotatory powers, and in the degree of hydration and the solubility of their calcium and barium salts, thus:

*Calcium salts.*

Dextronate  $Ca(C^6H^{11}O_7)^2 + H^2O$ , soluble in 34 parts of water at  $16^\circ$ .  
Gluconate  $Ca(C^6H^{11}O_7)^2 + 2H^2O$ , " 25 "

*Barium salts.*

Dextronate  $Ba(C^6H^{11}O_7)^2 + 4H^2O$ , soluble in  $5\frac{1}{2}$  parts of water at  $30^\circ$ .  
Gluconate  $Ba(C^6H^{11}O_7)^2 + 3H^2O$ , " 6 "

**DEYAMITTIN**. An indifferent substance obtained, on one occasion, in the preparation of buxino from the roots and stalks of *Cissampelos Pareira*, by extraction with warm water, and precipitation with soda. On treating the precipitate with hydrochloric acid, the dayamittin remained undissolved, and crystallised from hot alcoholic solution in microscopic hexagonal plates. When treated with sulphuric acid, these crystals assumed a splendid blue colour, which quickly passed through green into red, and then disappeared (Flückiger, *Zeitschr. f. Chem.* vi. 251).

**DIABANTACHRONNYN**. This name was given by K. Liebe (*Jahrbuch f. Mineralogie*, 1870, 1) to the mineral which gives the colour to the green diabases of the Voigtland and the Frankenwald. This mineral was regarded by Liebe, as a distinct species, but Keungott (*ibid.* 1871, 51) has shown that it is identical with chlorite (p. 323).

**DIABASE**. This rock, belonging to the greenstone family, is a compact mixture of one or two felspathic minerals with augite, and usually also finely divided chlorite. It is especially characterised by the entire absence of quartz, and the rarity of the presence of mica.

The felspathic constituents are the most abundant, and appear, sometimes in crystals more or less distinct, sometimes in tabular particles, sometimes massive, with a white, greenish-white, or greyish-white colour. They consist of a triclinic alkali-felspar, namely oligoclase, and a lime felspar probably labradorite. The augite is next in proportion, and has a granular, prismatic, or acicular structure, and usually a green or black-brown colour. The proportion of lime in diabase is equal to that of the magnesia and ferrous oxide taken together. The chlorite, which is the least abundant constituent, imparts to the rock its green colour, and impregnates it, usually in very fine earthy particles, sometimes in scales. When it is dissolved out by hydrochloric acid, the rock becomes paler in colour. The more fine-grained the mass, the greater is the quantity of chlorite contained in it.

Titaniferous iron ore, magnetic iron ore, and apatite, are also constant constituents of diabase, and calcium carbonate is usually present in imperceptibly small particles. Accessory constituents are iron pyrites, magnetic pyrites, copper pyrites, actinolite, asbestos, ferrous carbonate, axinite, epidote, olivine, hornblende, mica, diallage, and a few zeolites. The titaniferous iron, apatite, and chlorite, are more or less soluble in hydrochloric acid; the felspar and augite are insoluble.

Diabase forms beds and veins in the palaeozoic formations, occurring especially in Nassau, in the Hartz, the Voigtland, Upper Franconia, Westphalia, Devonshire and Norway. It is usually regarded as an eruptive rock, but sometimes occurs in strata, resembling the sedimentary deposits and passing into them.

Transitions from diabase to serpentine have also been observed, and, on the other



Locality.	Analyst.	Specific Gravity.	Strakonitz, Bohemia.	Knochen- dult, Moravia.	Staufenberg near Zorge, Hartz.	Hofgeiss, Hartz.	Laut- decken- berg, Hartz.	Nassau near Magne- sprung, Hartz.	Hedrichs- burg near Magne- sprung, Hartz.	Bos- trapp, Hartz.	Lapide Alten- harz.	Colberg, bach R. ad. near Weil- burg, Nassau.	Lehn- tunnel near Weilburg, Nassau.	Gälvineck near Weil- burg, Nassau.	Kupper- berg, Upper Franconia.	Rietz de Nassau, Madera.
Analyst.	Specific Gravity.		Tschermak. mak. 2.859	Tschermak. mak. 2.953	Schilling. 3.003	Schilling. 2.95	Schilling. 2.802	Carmichael. 3.031	Keibel. 2.994	Fuchs. 3.081	Kaysers. 3.081	Senfter. 2.948	Senfter. 2.918	Senfter. 2.995	Senfter. 2.969	Senfter. 2.79
Silica	51.73		45.80	45.26	45.20	46.60	46.60	47.17	48.86	46.26	47.36	46.04	48.62	41.17	45.03	49.15
Titanic oxide	—		trace.	—	—	—	—	—	—	—	0.51	1.46	1.86	3.08	0.33	0.83
Alumina	15.30		18.49	16.02	13.90	21.60	21.60	17.30	15.17	19.20	0.51	17.35	16.25	13.24	17.59	17.86
Chromic oxide	—		—	—	—	—	—	—	—	—	—	trace.	trace.	trace.	trace.	—
Ferric oxide	10.56		5.67	7.29	9.40	2.86	2.86	4.07	3.32	10.06	1.53	1.21	3.42	3.56	3.92	1.07
Ferrous oxide	3.38		4.90	7.09	4.92	6.40	6.40	5.81	6.71	10.20	7.93	10.59	9.12	12.50	7.80	10.77
Manganous oxide	—		—	—	—	—	—	0.57	0.35	—	0.44	—	—	trace.	trace.	0.75
Cobalt	—		—	—	—	—	—	—	—	—	—	—	—	trace.	—	—
Nickel	—		—	—	—	—	—	—	—	—	—	—	—	trace.	—	—
Zinc	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
Copper	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
Lead	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
Magnesia	3.20		5.74	6.40	7.80	6.48	6.48	5.59	7.56	5.52	6.53	6.41	4.93	8.21	6.13	3.24
Lime	6.61		12.70	8.11	12.44	9.25	9.25	14.10	11.34	9.17	10.08	5.56	5.91	10.24	10.66	6.57
Baryta	—		—	—	—	—	—	—	—	—	—	trace.	trace.	trace.	—	—
Soda	2.14		3.20	4.04	2.94	0.94	0.94	2.42	3.11	0.33	2.85	3.75	5.23	2.57	3.81	5.49
Potash	1.37		0.60	0.33	0.40	0.84	0.84	0.33	1.65	0.21	0.84	2.11	1.60	1.60	1.41	2.29
Water	4.85		3.24	3.60	3.16	3.10	3.10	3.71	2.46	0.53	3.05	3.70	3.36	3.21	3.30	1.21
Phosphoric anhydride	—		—	—	—	—	—	—	present.	—	0.26	0.64	0.36	0.53	0.33	0.99
Carbonic anhydride	—		—	—	—	—	—	—	—	—	0.18	0.35	0.13	0.64	0.50	trace.
Sulphuric anhydride	—		—	—	—	—	—	—	—	—	FeS <sub>1.96</sub>	trace.	trace.	trace.	trace.	—
Sulphur	—		—	—	—	—	—	—	—	—	—	0.09	—	0.09	0.12	—
Arsenic	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
Chlorine	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
Fluorine	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
Organic substance	—		—	—	—	—	—	—	—	—	—	—	—	—	—	—
	89.14		100.34	98.73	100.16	100.88	100.88	101.07	100.53	101.68	100.61	99.67	100.79	100.64	101.02	100.22

hand, alterations of it more or less advanced, are known, forming aphanites and other diabase conglomerates, and almond stones.

Diabase has a specific gravity of 2·8 to 3·1; begins to turn yellow when heated to 200°. It exhibits the following varieties of structure.

1. Fine-grained diabase. 2. Coarse-grained, resembling granite in appearance. 3. Porphyritic, containing crystals of labradorite, oligoclase and augite. 4. Compact, containing a considerable proportion of chlorite, and of grey-green, dirty-green, or blackish-green colour. 5. Slaty diabase, very rich in chlorite, and often very fine-grained.

The table on page 425 contains the most trustworthy analyses that have been made of diabase. (R. Souffier, *J. pr. Chem.* [2], vi. 227.)

**DIALLYLENE** (L. Henry, *Deut. Chem. Ges. Ber.* v. 449). When diallyl tetrabromide  $C^6H^4Br^2$  is heated with solid caustic potash, it is converted into dibromodiallyl,  $C^6H^4Br^2$ , and this product, heated with alcoholic potash, gives up 2HBr and is converted into the compound  $C^6H^6$  isomeric with benzene. This compound is called by Henry *diallylene*, a name which more properly belongs to the hydrocarbon  $C^6H^6$ , inasmuch as allylene is  $C^3H^4$ .

**DIAMIDOHYDRIN.** See CHORHYDRINS (p. 319.)

**DIAMYLENE.** See AMYLENE, (p. 64.)

**DIAPHORITE.** See FREISLEBENITE.

**DIASPORE.** R. Hermann (*J. pr. Chem.* [2], vi. 70) has analysed three varieties of diasporo from the emery vein near Miamarsk in the district of Katharinenburg, Russia: *a.* Brown-yellow, strongly lustrous laminae, grown together in cellular groups; *b.* Milk-white, yellowish or brownish, parallel-fibred, in narrow veins or threads in the emery, the fibres at right angles to the walls of the veins; *c.* Broadly laminated groups of grey colour:

	$Al^2O^3$	$Fe^2O^3$	$H^2O$	$P^2O^5$		Sp. gr.
<i>a</i>	77·95	6·60	15·00	0·45	= 100	3·40
<i>b</i>	77·90	6·50	14·00	1·60	= 100	3·23
<i>c</i>	67·15	5·00	15·00	12·85	= 100	3·35

All three varieties contain phosphoric acid, which has also been found by C. U. Shepard (*Sill. Am. J.* [2], 1, 96) in diasporo from Chester County, Pennsylvania. A well defined crystal of sp. gr. 3·343, semi-transparent, of hair-brown colour passing into violet, was found to contain 83·50 p.c.  $Al^2O^3$ , 0·38 FeO, 15·80  $H^2O$ , and 0·32  $P^2O^5$ , with traces of manganese.

**DIAZOBENZENE**,  $C^6H^5N^2$ . The nitrate of this base dissolves readily in a solution of potassium bisulphite, the liquid becoming hot, and sulphur dioxide being given off. On cooling, the liquid solidifies to a magma of yellow crystals, which, by recrystallisation from boiling water, are obtained in the form of colourless shining scales, having the composition  $C^6H^5KN^2SO^3 + H^2O$ . This salt does not explode when heated, and yields neither ammonia nor aniline when heated with soda-lime. Heated with nitric acid it yields sulphuric acid. When barium chloride is added to the hot solution, the salt  $Ba(C^6H^5N^2SO^3)^2$  separates, on cooling, in colourless hydrated crystals. When silver nitrate is added to the solution of the potassium salt, metallic silver is precipitated, and the yellow solution yields, on evaporation, fine yellow shining plates of a silver salt which explodes gently when heated (Strecker, *Deut. Chem. Ges. Ber.* iv. 784).

When diazobenzene-sulphonic acid is treated with potassium bisulphite, the acid  $C^6H^5N^2SO^3$  is formed according to the equation:

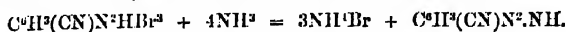


This acid crystallises from boiling water in colourless shining needles or plates; does not yield sulphuric acid when boiled with nitric acid; and gives off only half its nitrogen as aniline (or ammonia) when heated with soda-lime. Its *barium salt*  $Ba(C^6H^5N^2SO^3)^2 + 5H^2O$ , obtained by boiling the solution with barium carbonate, crystallises in long, lance-shaped, light yellow needles. The *lead salt*  $Pb(C^6H^5N^2SO^3)^2 + 2H^2O$  forms small white crystals. The acid reduces silver and mercury salts; its salts are isomeric with those obtained by the action of bisulphites on diazobenzene nitrate (Strecker).

**DIAZOCYANOBENZENE**,  $C^6H^5N^4$  =  $C^6H^5(CN)N^2$  (Griess, *Deut. Chem. Ges. Ber.* ii. 369). This compound is formed as a nitrate,  $C^6H^5N^4NO^3H$ , when amidobenzonitril (1st Suppl. 526) is treated with excess of nitric acid containing nitrous

# DIAZOCYANOBENZENIMIDE—DIBENZYL-SULPHUREA. 427

acid. The nitrate forms explosive needles or prisms, sparingly soluble in cold water. The solution gives, with platinum chloride, reddish-yellow needles of a platinumchloride, and with auric chloride an oil which solidifies in delicate laminae. With a solution of bromine in hydrobromic acid it forms a perbromide  $C^6H^4(CN)N^+HBr^-$  which crystallises in indistinct yellowish-red prisms, and when treated with aqueous ammonia is converted into diazocyanobenzonimide,  $C^6H^4(CN)N^+NH^-$ :



The platinumchloride, distilled with dry sodium carbonate, yields chlorobenzonitril,  $C^6H^4(CN)Cl$  (i. 564), in white needles melting at  $39^\circ$ .

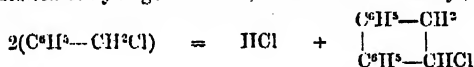
The aqueous solution of the nitrate, mixed with hydriodic acid, deposits iodobenzonitril or iodocyanobenzene,  $C^6H^4(CN)I$ , in white needles melting at  $41^\circ$ , smelling like bitter almond oil, insoluble in water, easily soluble in alcohol and in ether.

**DIAZOCYANOBENZENIMIDE**,  $C^6H^4(CN)N^+NH^-$ , formed by the action of aqueous ammonia on diazocyanobenzene-perbromide, is nearly insoluble in water but easily soluble in warm alcohol, from which it crystallises in long sulphur-yellow needles melting at  $57^\circ$ , and detonating when strongly heated (Griess).

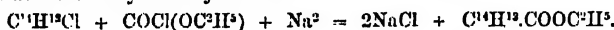
**DIAZOPHENOL**. See PHENOL DERIVATIVES.

**DIAZOPHENYL-PROPIONIC ACID**. See PHENYL-PROPIONIC ACID.

**DIBENZYL CARBOXYLIC ACID**,  $C^{12}H^{10}O_2 = C^{12}H^{12}.COOH$  (Wurtz, *Comp. rend.* lxx. 350). An acid produced by the action of sodium-amalgam on a mixture of benzyl chloride and ethyl chlorocarbonate, 2 mols. benzyl chloride probably uniting together, with evolution of hydrogen chloride, to form chlorodibenzyl,  $C^{12}H^{11}Cl$ :



and this compound being converted by the sodium and chlorocarbonic ether into the ethylic ether of dibenzylcarboxylic acid:



252 grams of benzyl chloride, 108 grams of chlorocarbonic ether, and 8 kilograms of 1 p.c. sodium-amalgam are placed in a flask provided with reversed condenser and heated in a salt-water bath till the mass becomes solid; water is then added, the whole shaken with ether, the ether distilled off, and the residuo saponified by heating it with potash to  $180^\circ$ . On adding an acid to the alkaline liquid a viscid mass separates, from which boiling water extracts dibenzylcarboxylic acid, to be purified by recrystallisation from water and alcohol.

Dibenzylcarboxylic acid is nearly insoluble in cold water, slightly soluble in boiling water, easily soluble in alcohol and ether. It melts at  $84^\circ$ , gives off aromatic and irritating vapours, and volatilises at a higher temperature. Its salts have but little inclination to crystallise. The calcium salt,  $Ca(C^{12}H^{12}O_2)^2$ , is soluble, and the solution when heated becomes covered with a film. The lead salt,  $Pb(C^{12}H^{12}O_2)^2$ , forms a thick white precipitate melting at  $146^\circ$ . The silver salt,  $C^{12}H^{12}AgO_2$ , exhibits similar characters. The calcium salt distilled with an equal weight of quick-lime gives off a mixture of stilbene and dibenzyl:



**DIBENZYLIC ACID**,  $C^{12}H^{12}O_2$ , is formed, together with other products, by heating benzoic acid to  $180^\circ$  for some hours. A deep red liquid then distils over, which solidifies on cooling to an amorphous mass. This substance dissolves easily in alcohol, and the solution yields a number of crystallised bodies, amongst which are dibenzyllic acid, benzophenone, and a body having the composition  $C^{12}H^{12}O_2$ . Benzoic acid heated with phosphoric anhydride, also yields dibenzyllic acid, together with a viscid non-crystallising oil which, when heated with water to  $200^\circ$ , or when boiled, is reconverted into benzoic acid (Jena, *Ann. Ch. Pharm.* clv. 77).

**DIBENZYL-GUANIDINE**. See GUANIDINE.

**DIBENZYL-PHOSPHINE**. See PHOSPHINES.

**DIBENZYL-UREA**. See BENZYL UREAS (p. 181).

**DIBENZYL-SULPHUREA**, or **DIBENZYL-SULPHOCARBAMIDE**,  $CS(NH.C^6H^5)_2$ , is formed by heating an alcoholic solution of benzylamine in a flask

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with reversed condenser as long as hydrogen sulphide is given off. On evaporating and repeatedly crystallising the residue from alcohol, dibenzyl-sulphurea is obtained in large four-sided shining plates. It melts at  $114^{\circ}$ , dissolves in alcohol and ether, but is insoluble in water. When heated with mercuric oxide, it is converted into dibenzyl-urea (Strakosch, *Deut. Chem. Ges. Ber.* v. 692).

**DIBROMODIPHENYLCARBAMIDE.** See PHENYLCARBAMIDES.

**DIBROMONITROPHENOLS.** See PHENOL DERIVATIVES.

**DIBUTYRALDINE**,  $C^4H^7NO$ . A base formed by the union of 2 mols. butyric aldehyde  $C^4H^8O$ , and 1 mol. ammonia  $NH^3$ , with elimination of  $H^2O$ . It is obtained, together with tetrabutyraldine, by treating butyraldehyde with alcoholic ammonia for two months at  $30^{\circ}$ , or for one day at  $100^{\circ}$ . The mode of separating these bases and obtaining coneine from the dibutyraldine has been already described (p. 380). Neither dibutyraldine nor tetrabutyraldine appears to have been obtained in the pure state (Schiff, *Ann. Ch. Pharm.* clvii. 352; *Deut. Chem. Ges. Ber.* v. 42).

**DICARBONAPHTHALIC ACID**,  $C^{10}H^4(CO^2H^2)^2$ , is obtained by boiling diquinonaphthalene (from bromonaphthalene-sulphonic acid) with potash-ley, and precipitating with hydrochloric acid. In the pure state it forms microscopic nearly colourless needles, which do not melt at temperatures near  $240^{\circ}$ . It is nearly insoluble in boiling water, but dissolves more easily in alcohol. Its barium salt,  $C^{10}H^4(CO^2)^2Ba + 2H^2O$ , forms small granular crystals, very soluble in water. The solution gives, with ferric chloride, a light yellow precipitate of an iron salt nearly insoluble in hot water. The copper salt separated in like manner forms groups of small needles; the lead and silver salts are sparingly soluble precipitates (Darmsstädter u. Wichelhaus, *Jahresb.* 1869, 477).

**DICARBONYL CHLOROPLATINITE.** See PLATINUM CHLORIDES.

**DICARBOTETRAPHENYL-TOLUYLENE-HEXAMINE.** See GUANIDINE.

**DICHLORETHYL OXIDE.** See ETHYL OXIDE.

**DICHLORHYDRIN.** See CHLORHYDRINS.

**DICHLOROMIONONTRIN.** See NITRINS.

**DIDENLACTAMIC ACID.** See LACTAMIC ACID.

**DIDYMIUM.** This metal has been detected in pyremorphite from Cumberland (C. Horne, *Chem. News*, xxvi. 109).

This method given by Erk (*Zeitschr. f. Chem.* [2], vii. 100), for the separation of cerium from didymium and lanthanum has been already described (p. 273). To separate didymium from lanthanum, the solution containing the two metals is precipitated to the extent of one half with ammonia, and the washed precipitate is left for a day at the ordinary temperature in contact with the rest of the solution, the whole being frequently stirred: the lanthanum, being the stronger base, then passes into the solution in predominant quantity. The lanthanum solution thus obtained is again half precipitated and treated as above. After the second treatment, the solution gives but slight indications with the spectroscope of the absorption-bands of didymium, and after four such fractional precipitations, the didymium lines are no longer visible in a column of the solution 30 centimeters long. The solutions rich in didymium are treated in the same manner, and the intermediate solutions are mixed together and separately treated. A didymium solution is regarded by Erk as free from lanthanum, when, on precipitating the greater part of the oxide with ammonia, and treating it as above, no difference of colour or of atomic weight can be found between this precipitate and the oxide precipitated from the filtrate.

For the separation of didymium and the other cerium metals from yttrium, Erk makes use of the property possessed by the cerium metals of forming sparingly soluble double sulphates, whereas the corresponding yttrium salt is easily soluble (i. 833). The whole of the cerium, and the greater part of the lanthanum having been separated as above, the didymium oxide is dissolved in nitric acid, and boiled with a moderately concentrated solution of sodium sulphate, and the same treatment is repeatedly applied both to the precipitated didymium sulphate, and to the oxides which remain in solution, whereby the whole of the didymium is ultimately obtained in the precipitate, and the yttrium in the solution. In the separation of didymium from lanthanum, the yttrium is found chiefly in the solutions of didymium most free from lanthanum.

**Salts.**—The chloride crystallises from aqueous solution, according to Hermann (*J. pr. Chem.* lxxxii. 385), in granular masses containing  $DiCl^2 + 4H^2O$ . Zschiesche, on the

other hand (*ibid.* cvii. 65), obtained distinct monoclinic crystals which, after drying over oil of vitriol, had the composition  $\text{DiCl}^2 + 5\text{H}^2\text{O}$ . The *nitrate* crystallises with  $4\text{H}^2\text{O}$ . The *sulphate* crystallised from warm water has, according to Zschiescho, the composition  $\text{DiSO}^4 + 3\text{H}^2\text{O}$ , whereas, according to Hermann, Marignac and Rammelsberg, it contains  $\text{DiSO}^4 + \frac{1}{2}\text{H}^2\text{O}$ . To the dark brown *peroxide* Hermann assigned the formula  $\text{Di}^2\text{H}^{21}$ . Zschiescho doubts this formula, especially as this oxide is converted by strong ignition into the ash-grey monoxide—so that it is scarcely possible to obtain the peroxide quite pure by ignition in the air.

**Absorption-spectrum.**—A concentrated solution of pure didymium nitrate, 4 centimeters deep, exhibits a spectrum containing seven dark bands, the relative positions of which are seen in figure 13, the letters in the upper line indicating some of the principal Fraunhofer lines, D coinciding with 42 on the scale.

This spectrum agrees in the main with that described by Bahr and Bunsen (*Ann. Ch. Pharm.* cxxxvii. 1).

The smaller the quantity of didymium in solution, the fewer are the dark bands seen. In very dilute solutions, only the band 45 in the yellow and 64 in the green (observed some time ago by Gladstone, ii. 322), are visible, and of these the former is always the stronger. These two bands afford the best indication of the presence of didymium in a lanthanum solution (Erk).

**Equivalent and Atomic Weights.**—To determine the equivalent weight of didymium, Erk precipitated a weighed quantity of the anhydrous sulphate with ammonium oxalate, and ignited the oxalate strongly before a gas blowpipe flame till it acquired a constant weight (the loss of weight of the platinum crucible by ignition being taken into account). The equivalent weight thus determined was  $\text{Di} = 47.45, 47.43$  and  $47.82$ . Zschiescho (*J. pr. Chem.* cvii. 65), from the analysis of the sulphate, found the numbers 46.885, 46.72, 47.68, 47.93 and 48.08, the highest of which he regards as the most exact. As a mean of all these determinations the number 47.5 may be regarded as a very near approximation to the true equivalent weight of didymium.

If, then, didymium be regarded, according to the ordinary view, as a dyad metal, forming the compounds  $\text{DiCl}^2$ ,  $\text{DiO}$ , &c., its atomic weight will be 95. Mendelejeff, however, for reasons already explained (see CERITE METALS, p. 273), regards the sulfifiable oxide of didymium as a sesquioxide,  $\text{Di}^2\text{O}^3$ , and accordingly assigns to didymium an atomic weight equal to three times its equivalent weight, that is  $3 \times 47.5 = 142.5$  [or 138, if the older equivalent 46 be adopted]. According to this view the hydrate of didymium will be  $\text{Di}(\text{OH})^3$  instead of  $\text{Di}(\text{OH})^2$ ; the chloride  $\text{DiCl}^3.6\text{H}^2\text{O}$  instead of  $\text{DiCl}^2.4\text{H}^2\text{O}$ , the sulphate  $\text{Di}^2(\text{SO}^4)^2.8\text{H}^2\text{O}$  instead of  $3\text{DiSO}^4.8\text{H}^2\text{O}$ , and the double sulphates will have formulæ analogous to the alums, e.g.  $\text{DiK}(\text{SO}^4)^2.\text{H}^2\text{O}$ .

Mendelejeff's reasons for the proposed alterations in the atomic weights of the cerium metals, together with Rammelsberg's objections to them, have been already considered (p. 273).

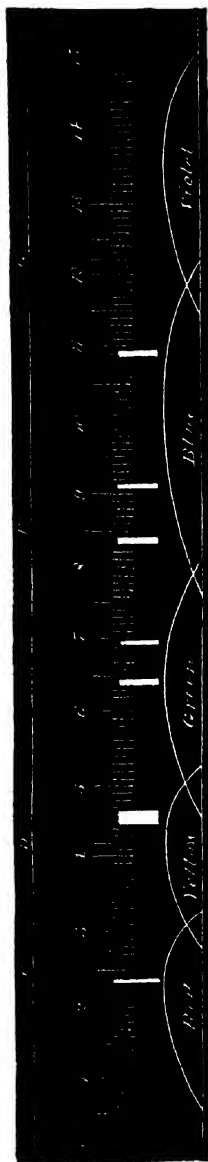
**DIETHOXYL - DIETHESULPHYL - PYROSULPHOPHOSPHORIC ETHER.** See PYROSULPHOPHOSPHORIC ETHERS.

**DIDETHYLDIACETAMIDE.** See ETHYLDIACETIC ACID.

**DIDETHYLACETONE.** Syn. with DIPROPYL KETONE (q. v.)

**DIDETHYL-DIOXYBENZOIC ACID.** See DIOXYBENZOIC ACID.

FIG. 13.



## 430 DIETHYLIDENE-LACTAMIC ACID—DIGESTION.

**DIETHYLIDENE-LACTAMIC** and **DIETHYLENE-LACTAMIC ACIDS.** See LACTAMIC ACID.

**DIETHYL-PHOSPHINIC ACID.** See PHOSPHINIC ACIDS.

**DIETHYL-SULPHUREA.** See SULPHOCARBANIDES.

**DIFFUSION.** See GASES.

**DIGALLIC ACID.** See TANNIC ACIDS.

**DIGESTION, ANIMAL.** (Kühne, *Physiologische Chemie*, Bd. I.; Schiff, *Sur la Physiologie de la Digestion*).

The action of saliva upon raw starch is very incomplete (Schiff), for while it is capable of converting boiled starch completely into dextrose, it acts only upon the 'granulose' of raw starch, leaving the 'cellulose' layers of the granules quite unchanged.

In spite of much attention during the last few years, the digestion of proteids in the stomach is still very imperfectly understood, neither the exact products nor the theory of the process being at all clear. The products vary somewhat with the proteid digested, and with the quantity of pepsin or free acid in the digestive fluid, but, speaking broadly, they consist of several diffusible forms of proteid, known as *peptones*, and an indiffusible form—*parapeptone*—which is insoluble in water, but soluble in dilute acids or alkalis, and, in fact, appears to agree in all its properties with syntonin, except that it is incapable of undergoing peptic digestion. Thus, if boiled blood fibrin be submitted to artificial peptic digestion, a solution is obtained, which is at first opalescent, but by longer digestion becomes clear, and on neutralisation yields a precipitate of *parapeptone*.

The filtrate from this precipitate contains three forms of peptones—known as Meissner's *a*, *b*, and *c* peptones. The *a*-peptone is characterised by being precipitated by nitric acid, and, in a solution slightly acidulated with acetic acid, by potassic ferrocyanide; the *b*-peptone is not precipitated by nitric acid, and by potassic ferrocyanide only in a solution strongly acidulated with acetic acid; and the *c*-peptone is precipitated by neither of the above reagents. (For the general properties common to all peptones, see **PROTEIDS**.) Sometimes an additional, non-diffusible form of proteid—*metapeptone*, is present in the solution; it appears to be imperfectly formed peptone; by prolonged digestion, part of the *parapeptone* is converted into another body, *dyspeptone*, which is insoluble in solutions containing the same percentage of free acid as gastric juice, and is accordingly precipitated as it is formed.

According to Meissner, the process of peptic digestion consists first, in the formation of a solution containing a form of proteid insoluble in pure water, whether or not the original proteid was soluble, and then in the splitting up of this product, into *parapeptone* and the *a*, *b*, and *c* peptones, of which latter he considers the *c*-peptone the final or most complete form. This view is, however, opposed by the fact that the quantities of *parapeptone* and peptones bear no constant ratio to one another, but vary almost indefinitely with the strength of the digestive fluid, the temperature at which the process is carried on, &c.; and as all the products of peptic digestion can be obtained from proteids by simple prolonged boiling with pure water, the pepsin is, perhaps, rather to be regarded as a ferment, active in acid solutions only, and capable of adding the elements of water to proteid bodies, and causing them to break up in various ways.

With other proteids than blood fibrin the process of peptic digestion is similar in the main, though in some cases the peptones and *parapeptone* produced present slight differences. Raw white of egg digests only after previous conversion into syntonin, a process which is very slow under the conditions obtaining in the stomach (Kühne), boiled white of egg digests without undergoing this previous change. Syntonin under peptic digestion yields, besides the *a*, *b*, and *c* peptones, a fourth form which differs from them in being precipitated from its solution by cupric sulphate. The coagulation of the casein of milk which occurs in the stomach is not due to the free acid, for it is produced equally well by neutralised gastric juice (Schiff); neither is it due to the pepsin, but as boiled gastric juice loses this power, it is probably due to some other ferment not yet isolated.

Peptic digestion is at once checked when the food enters the intestine; this is due chiefly to the bile, which not only renders the chyme alkaline, but precipitates any peptones it may contain in solution, and these, in falling, carry the pepsin down with them mechanically (Burkard).

In the small intestine the digestion of proteids is mainly carried on by the pancreatic secretion, which, besides its ferments converting starch into glucose and breaking

up fats, contains a third, which in alkaline solution first converts ordinary proteids into peptones, and then by further action breaks them up, tyrosin being one of the chief products.

The secretion of the mucous membrane of the small intestine, which is obtained pure by Thiry's method (*Wien. Akad. Ber.*, Bd. I.), according to most observers, dissolves fibrin, but no other proteid (Thiry, Leube, Schiff); it also readily converts starch into glucose, and in the dog, rabbit, and pig contains an additional ferment which converts cane-sugar into glucose, but which is absent in the sheep and calf (Paschutin).

The question of the changes which fats undergo in the alimentary canal is still very obscure; a part of them is no doubt saponified, but it seems probable that the greater portion will ultimately be found to undergo no chemical decomposition, but to be simply emulsified by the bile and pancreatic juice and then directly ingested as small molecules by the epithelial cells, and passed on by them to the commencing lacticals.

H. N. M.

**DIGLYCOLLAMIC DIURAMIDE.** See DIURAMIDES.

**DIGLYCOLLIC ACID.** On the constitution of this acid, see Kolbe (*J. pr. Chem.* [2], ii. 386; Heintz, *ibid.* iii. 69, 120; Claus, *ibid.* iii. 123).

**DIHYDRACRYLIC ACID.** See HYDRACRYLIC ACID.

**LACTAMIC ACID.** See LACTAMIC ACID.

**BILL CARVOL.** See OILS VOLATILE.

**DIMETHYL.** See METHYL.

**DINONYL KETONE.** Syn. with CAPRONE (p. 251).

**DIOPSIDE.** Chrome-diopside from the olivine rock of the basalt of the Dreiser Weiher in the Eifel, contains, according to Rammelsberg (*Pogg. Ann.* cxli. 516),

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Cr <sup>2</sup> O <sup>3</sup>	MgO	CaO	FeO
49.71	7.42	2.61	17.84	17.39	5.03 = 100.

These numbers may be represented by the formula  $11\text{RSiO}^2(\text{Al}; \text{Cr})^2\text{O}^3$ , in which  $11\text{R} = \text{Fe} + 6\text{Mg} + 4\text{Ca}$ .

**DIOSMOSE.** See OSMOSE.

**DIOXYBENZOIC ACIDS, C<sub>7</sub>H<sub>4</sub>O<sub>4</sub>.** This formula includes protocatechuic, carbohydroquinonic, and hypogallic acids (iii. 239).

(1.) *Protocatechuic acid* has been shown by Barth to be producible both from oxybenzoic and from paraoxybenzoic acid (1st Suppl. 976; also *Deut. Chem. Ges. Ber.* v. 633; *Chem. Soc. J.* [2], ix. 829), namely, by converting the oxybenzoic into a sulphybenzoic acid by treatment with sulphuric acid, and decomposing the latter with potash. The quantity of protocatechuic acid produced from paraoxybenzoic acid is, however, much less than that from oxybenzoic acid, a less soluble acid, which gives a red reaction with ferric salts, being formed at the same time, probably by the action of the potash on an isomeric sulpho-acid.

Assuming, now, that the radicals CO<sup>2</sup>H and OH occupy in paraoxybenzoic acid the positions 1 : 4, and in oxybenzoic acid 1 : 3, the positions in protocatechuic acid must be 1 : 3 : 4, thus :

		6	5	4	3	2	1
Oxybenzoic	C <sup>6</sup>	H	H	H	OH	H	CO <sup>2</sup> H
Paraoxybenzoic	C <sup>6</sup>	H	H	OH	H	H	CO <sup>2</sup> H
Protocatechuic	C <sup>6</sup>	H	H	OH	OH	H	CO <sup>2</sup> H.

Now protocatechuic acid, when subjected to dry distillation, yields always, and solely, pyrocatechin. Hence, if the above formula of protocatechuic acid be correct, the two hydroxyls in pyrocatechin must be attached to contiguous carbon-atoms (3 : 4 or 1 : 2), and in that case, since these radicals occupy in resorcin the positions 1 : 4, they must have, in hydroquinone, the positions 1 : 3. On the other hand, if, as Gräbe supposes, the position formula of hydroquinone is 1 : 2, then that of pyrocatechin must be 1 : 3 (or 2 : 4), that of pyrocatechuic acid must be 1 : 2 : 4, and that of oxybenzoic acid 1 : 2. The latter view, however, is contradicted by Meyer's experiments (p. 133), which have shown that the position-formula of salicylic acid is 1 : 2, and that of oxybenzoic acid 1 : 3.

*Dimethylprotocatechuic acid* is prepared by heating 1 gram of protocatechuic acid, 4 grams of methyl iodide, and 1 gram of pure potassium hydrate with methyl alcohol, in a sealed tube to 140° for some hours. The liquid portion is filtered from the

potassium iodide, the alcohol evaporated off, and the oily residue boiled for some time with dilute soda-ley. After cooling, the liquid is acidulated with sulphuric acid, by which means a flocculent deposit of the new acid is produced. This is shaken up with ether, and the insoluble residue repeatedly crystallised from water. It is obtained in

glistening white needles having the composition  $C^6H^3 \begin{cases} COOH \\ OCH^3 \\ OCH^3 \end{cases}$ . It melts at  $170^\circ-171^\circ$ ,

and does not show the characteristic iron reaction of protocathechuic acid. By distillation with lime, it gives rise to an oil, boiling between  $210^\circ$  and  $215^\circ$ , and having the composition of dimethyl-pyrocatechin:  $C^6H^4(OCH^3)_2$ .

The acid is converted by bromine into bromodimethyl-protocatechuic acid,  $C^6H^2Br.(OCH^3)_2.COOH$ , which crystallises from water in needles.

Diethylprotocatechuic acid  $C^6H^3 \begin{cases} COOH \\ OC^2H^5 \\ OC^2H^5 \end{cases}$  is prepared in a similar manner to the

dimethyl-acid. It melts at  $149^\circ$ , and gives no reaction with ferric chloride. By dry distillation it yields an oil, probably consisting of diethyl-pyrocatechin. With bromine, it forms a crystalline product, exhibiting the composition of a mixture of mono- and di-bromodimethyl-pyrocatechuic acid (R. Koelle, *Ann. Ch. Pharm.* clix. 249).

(2.) *Dioxybenzoic acid*, 1 : 2 : 4 (Max Ascher, *Deut. Chem. Ges. Ber.* iv. 649). This modification is produced by a series of transformations from paranitrotoluene,  $C^6H^4(NO^2)HH(CH^3)$ . This body, treated with fuming sulphuric acid, is converted

into nitrotoluene-sulphonic acid  $C^6H^3 \begin{cases} CH^3 \\ SO^3H \\ NO^2 \end{cases}$ , in which, also, the radicles  $CH^3$  and

$NO^2$  occupy the paraposition 1 : 4. To determine the relative positions of the radicles  $CH^3$  and  $SO^3H$ , the nitrosulpho-acid was converted into the corresponding amido-sulpho-acid, and this into the diazo-compound by treatment with nitrous acid under alcohol; and the diazo-compound was boiled with absolute alcohol under pressure, whereby the nitrogen was eliminated and replaced by hydrogen. By this means, a toluene-sulphonic acid is produced, the potassium salt of which, when fused with potash, yields a liquid cresol, and this, when extracted with ether and repeatedly fused with potash, is converted into salicylic acid. Now in salicylic acid, as appears from Meyer's experiments (p. 133), the relative position of the radicles  $CH^3$  and  $OH$  is 1 : 2; this, therefore, must also be the position of the  $CH^3$  and  $SO^3H$  in the toluenesulphonic acid from which it was obtained, and therefore, the position of the  $CH^3$ ,  $SO^3H$ , and  $NO^2$  in the nitrotoluenesulphonic acid must be 1 : 2 : 4.

		6	5	4	3	2	1.
Salicylic acid . . . . .	$C^6$	H	H	H	H	(OH)	( $CH^3$ )
Toluenesulphonic acid . . .	$C^6$	H	H	H	H	( $SO^3H$ )	( $CH^3$ )
Nitrotoluenesulphonic acid .	$C^6$	H	H	( $NO^2$ )	H	( $SO^3H$ )	( $CH^3$ )

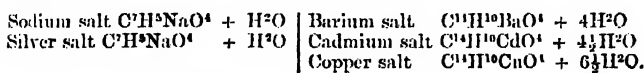
To convert this nitro-acid into dioxybenzoic acid, it was first converted, as above, into the corresponding amido-acid, then into the diazo-compound. The latter is soluble in water, insoluble in alcohol, not easily acted upon by alkalis, detonates slightly when heated upon platinum foil. When boiled with water, it gives off nitrogen, and is converted into a cresolsulphonic acid  $C^6H^4(OH)H(SO^3H)(CH^3)$  or 1 : 2 : 4; and by fusing the potassium salt of this acid with potash, the sulphuric acid residue  $SO^3H$  is replaced by  $OH$ , and at the same time the methyl-group  $CH^3$  is oxidised to carboxyl, the product being the corresponding dioxybenzoic acid  $C^6H^4(OH)_2(COOH)$ .

To extract the acid, the fused mass is acidulated and shaken with ether, and the ether left to evaporate, whereby the acid is obtained in needles still retaining phenolic impurities. To purify it, the ethereal residue is dissolved in water, the filtered solution precipitated with lead acetate, and the lead precipitated by hydrogen sulphide, the impurities being thereby removed from the solution, together with the lead sulphide. The filtrate is a colourless liquid from which the para-dioxybenzoic acid may be extracted with ether. It crystallises in stellate groups of needles which contain 3 mols. water, and melt at  $148^\circ$ . When dried at  $120^\circ$  it gives off all its water of crystallisation, and the dehydrated acid melts at  $194^\circ$ . It sublimes readily in small white needles, which also melt at  $194^\circ$ ; dissolves readily in water, alcohol, and ether, and produces with ferric chloride a fine red-brown coloration. These characters sufficiently distinguish this modification of dioxybenzoic acid from protocathechuic acid, which crystallises with 1 mol. water, gives off its water at  $100^\circ$ , melts in the dehydrated state at  $199^\circ$ , and gives with ferric chloride a dark blue-green reaction. *Hypogallie acid* (iii. 239°), also gives a blue colour with ferric chloride, crystallises with  $1\frac{1}{2}$  mol. water, becomes anhydrous at  $100^\circ$ , and melts at about  $180^\circ$ . *Carbohydro-*



*quinonic acid* (iii. 214), crystallises with 1 mol. water, which it gives off at  $100^{\circ}$ , melts at  $207^{\circ}$  (corr.) and is insoluble in ether. *Oxy-salicylic acid*, obtained by boiling mono-iodo-salicylic acid with potash (iv. 320), crystallises in anhydrous needles which melt at  $193^{\circ}$ , and gives a deep blue coloration with ferric chloride. All these acids are, therefore, distinct from dioxybenzoic acid 1 : 2 : 4.

Karst n. Senhofer (*Ann. Ch. Pharm.* clix. 217; clxiv. 109), have obtained another modification of dioxybenzoic acid, probably 1 : 3 : 6, by the action of melting potash on the potassium salt of disulphobenzoic acid (produced by heating benzoic acid with hydrogen sulphate and phosphoric anhydride to  $250^{\circ}$  in sealed tubes). On treating the fused mass with an acid, exhausting with ether, and evaporating the ethereal solution, the dioxybenzoic acid is obtained in long prisms very soluble in hot water, also in alcohol and ether. It is distinguished from protocatechuic acid by its crystalline form, by not giving the blue-green coloration with ferric chloride, and not being precipitated by neutral lead acetate. In the air-dried state it contains  $(C^6H^3(OH)^2.COOH + 14H^2O)$ ; it gives off its water at  $105^{\circ}$ , and melts at a temperature above  $220^{\circ}$ . Heated with strong sulphuric acid, it dissolves to a red liquid, which deposits a green powder on addition of water. Its salts crystallise moderately well; most of them give off their water of crystallisation at  $105^{\circ}$ , the copper salt, however, retains a portion of it even at  $110^{\circ}$ ;



The *ethyl ether*  $C^6H^3(C^2H^5O)^1$  prepared by passing hydrogen chloride into an alcoholic solution of the acid, remains on evaporation as a syrup which crystallises from water in groups of long prisms having a vitreous lustre. It melts at  $100^{\circ}$ , and remains transparent and amorphous for a long time after cooling.

This modification of dioxybenzoic acid differs from all those previously known, in not yielding by dry distillation any of the known dihydroxylbenzenes, but a yellow body called anthrachryson,  $C^{14}H^6O^8$ , formed from it by dehydration and condensation:  $2C^6H^3O^4 - 2H^2O = C^{14}H^6O^8$ . This body, which is also formed by heating the dioxybenzoic acid to  $120^{\circ}$ – $140^{\circ}$  with sulphuric acid, is, in fact, a tetra-oxyanthraquinone, and its formation is analogous to that of rufigallie acid from gallic acid, and that of rufopin from opianic acid (p. 86).

*Monobromodioxybenzoic acid*,  $C^6H^3BrO^4$ , is produced by adding a sufficient quantity of bromine-water to a cold aqueous solution of the last-mentioned modification of dioxybenzoic acid. On evaporating the solution and crystallising the residuum from hot water, monobromodioxybenzoic acid is obtained in colourless needles an inch long, melting at  $253^{\circ}$ . Its solution gives a brownish precipitate with ferric chloride, but it is not precipitated by lead acetate. The crystallised acid contains one molecule of water, which it loses at  $120^{\circ}$ . It is tribasic. Its *silver salt*,  $C^6H^3Ag^3BrO^4$ , is a yellow amorphous precipitate obtained by adding silver nitrate to the ammonium salt. The *barium salt* is readily soluble in water, and crystallises in long needles. The *copper salt* separates from a hot solution in light green, microscopic, but well-defined prisms  $(C^6H^3BrO^4)^2Cu + 8H^2O$ . The *potassium salt* crystallises in needles and dissolves very readily in water.

By fusing the monobrominated acid with potash, a large quantity is converted into dioxybenzoic acid, and a smaller quantity into gallic, trioxybenzoic, or dioxy-salicylic acid.

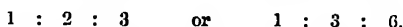
*Tribromodioxybenzoic acid*,  $C^6H^3Br^3O^4$ , is produced, together with a small quantity of the monobrominated acid, by tritulating dioxybenzoic acid with bromine. The mass becomes semifluid, hydrogen bromide is given off, and after the excess of bromine has been expelled over the water bath, the tribrominated acid remains as a yellowish crystalline mass, which dissolves easily in water, and separates therefrom in large tabular, anhydrous crystals melting at  $183^{\circ}$ . By fusion with potash, it is almost wholly reconverted into dioxybenzoic acid, together with a small quantity of a compound which gives a green colour with ferric chloride.

*Diethyldioxybenzoic acid*,  $C^6H^4(C^2H^5O)^2$ , is produced by heating the ethylic ether of dioxybenzoic acid with ethyl iodide, caustic potash, and a little alcohol in sealed tubes to  $130^{\circ}$  for some hours. The ethylic diethyl-dioxybenzoate thus formed is an oily liquid which is readily decomposed by boiling it with potash; and by acidulating the resulting alkaline solution with sulphuric acid, agitating with ether, and evaporating the ethereal solution, the free acid is obtained as an oily liquid, which soon solidifies to a crystalline mass, and crystallises from water in needle-shaped prisms melting at  $87^{\circ}$ – $88^{\circ}$ . The barium salt has the composition  $(C^6H^4O^4)^2Ba$ .

By heating diethyl-dioxybenzoic acid with quicklime, an oil is obtained boiling  $2nd\ Sup.$

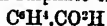
between 200°–260°, containing probably the diethylic ether of resorcin. The latter compound is easily obtained by heating resorcin with ethyl iodide and potash; it is an oily liquid boiling at 250° and giving no colour with ferric chloride. By heating it with hydriodic acid it is not reconverted into resorcin, but a resinous body is produced, the alkaline solution of which exhibits, even when very dilute, a strong dichroism, appearing green in reflected light and yellowish-red by transmitted light. Exactly the same reaction is shown by the distillate of a mixture of diethyl-dioxybenzoic acid and lime.

*Constitution of the Dioxybenzoic acid obtained from Disulphobenzoic acid.*—The monobrominated derivative of this acid fused with potash, yields gallic acid,  $C^7H^3O^5$ , which has also been formed synthetically from di-iodosalicylic and monobromoprotocatechuic acid. Admitting then, that in salicylic acid the hydroxyl groups occupy the positions 1 : 2, and in protocatechuic acid, the places 1 : 3 : 4, it follows that the constitutional formula of gallic acid must be either 1 : 2 : 3 : 4, or 1 : 3 : 4 : 6. Further the disulphobenzoic acid from which the dioxybenzoic acid under consideration is prepared is converted by fusion with sodium formate into isophthalic acid (1 : 3); consequently one of the groups  $SO^2H$  in this acid, and therefore the corresponding hydroxyl in the dioxybenzoic acid, must occupy the position 3. Hence it appears that the only possible relative positions for the carboxyl and hydroxyl in this dioxybenzoic acid, are



Of the six possible arrangements indeed 1 : 2 : 4 is excluded as belonging to Ascher's dioxybenzoic acid (p. 432); 1 : 3 : 4 as belonging to protocatechuic acid; and 1 : 2 : 6 cannot easily be reconciled with the formation of isophthalic acid. Finally 1 : 3 : 5 is inconsistent with the formation of gallic acid. Between the two remaining formulae 1 : 2 : 3 and 1 : 3 : 6 the results hitherto obtained by Barth and Senhofer do not enable them to decide with certainty, but from experiments not yet completed, they regard the latter as the more probable of the two.

**DIOXYMETHYLENE**,  $C^8H^4O^2$ . This compound, which Butlerow obtained by the action of silver oxide or oxalate on methyl iodide, and by the dry distillation of ethyl-glycollic acid (iii. 1006), is also produced by the dry distillation of glycollic acid itself. This acid, heated first to 120°, then for several hours to 160°, and finally for a day to 200°–220°, yields a carbonaceous residue, and a solid sublimate consisting of dioxymethylene (Krapsky, *Zeitschr. f. Chem.* vi. 178). According to Girard (*Bull. Soc. Chim.* [2], xiv. 217) it is also produced by heating methylene sulphide  $CH_2S$  to 170° in a closed vessel with sulphate or borate of silver.



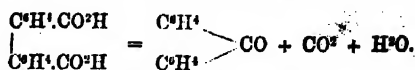
**DIPHENIC ACID**,  $C^{14}H^{10}O^4 =$   $C^{14}H^8.CO^2H$ . This acid is a product of the

oxidation of phenanthrene-quinone  $C^{14}H^8O^2$  (p. 93), and is always obtained in small quantity in the preparation of the latter. It is most conveniently prepared by heating the impure hydrocarbon containing anthracene with chromic acid solution, and crystallising the mixture of the quinones from alcohol, in order to remove an amorphous substance. The quinones are again treated with the oxidising mixture, which does not act on anthraquinone, and the acid is extracted from the product by ammonia.

Diphenic acid is sparingly soluble in cold water, more freely in hot water, and readily in alcohol and ether; it crystallises on quickly cooling the solution, in small shining plates, but if the solution cools down slowly, it is obtained in transparent compact anhydrous prisms; it separates also in the latter form on allowing an alcoholic solution to evaporate. By the evaporation of a solution in dilute alcohol, it was once obtained in very large transparent crystals containing two molecules of water. It melts at 226°, and sublimes in long transparent needles; when heated above its melting point, it blackens and decomposes. It is a strong bibasic acid.

*Barium diphenate*,  $C^{14}H^8BaO^4 + 4H^2O$ , is readily soluble in water and forms large transparent crystals. *Calcium diphenate*,  $C^{14}H^8CaO^4 + 2\frac{1}{2}H^2O$ , is a very soluble salt and does not crystallise well. *Magnesium diphenate*,  $C^{14}H^8MgO^4 + 4H^2O$ , crystallises in plates. *Silver diphenate*,  $C^{14}H^8Ag^2O^4$ , is a bulky white precipitate dissolving in a large quantity of hot water.

Diphenic acid heated with excess of quick lime, is converted, not into diphenyl, as might have been expected ( $C^{14}H^{10}O^4 - 2CO^2 = C^{14}H^{10}$ ), but into diphenylene ketone  $C^{14}H^8O$ :

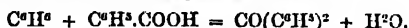


(Fittig & Ostermayer, *Ann. Ch. Pharm.* clxvi. 361).

**DIPHENINE.** This compound, which Laurent & Gerhardt obtained by reduction of dinitrozobenzene with hot alcoholic ammonium sulphide (ii. 336) is generally regarded as diamido-azobenzene  $C^{12}H^{12}N^4 = C^{12}H^8N^2(NH^2)^2$ ; but from the experiments of Lermontoff (*Deut. Chem. Ges. Ber.* v. 231), it appears to be really diamido-hydrazo-benzene  $C^{12}H^{12}N^4 = C^{12}H^{10}N^2(NH^2)^2$ , formed by addition of  $H^2$  to diamido-azobenzene (see HYDRAZOBENZENE).

**DIPHENYL.** See PHENYL.

**DIPHENYL KETONE**,  $CO(C^6H^5)^2$ , is formed, together with a small quantity of a substance which boils at a very high temperature, by heating a mixture of benzoic acid and benzoic acid to  $180^\circ$ – $200^\circ$  with phosphorus pentoxide:



No ketone is formed by heating benzoic acid alone with phosphorus pentoxide, and benzene alone is not acted upon at all (Kollarits & Merz. *Deut. Chem. Ges. Ber.* v. 447).

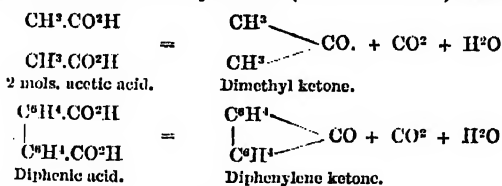
**DIPHENYL-ALLOPHANIC ETHERS.** See CYANIC ETHERS (p. 408).

**DIPHENYLAMINE.** See PHENYLAMINES.

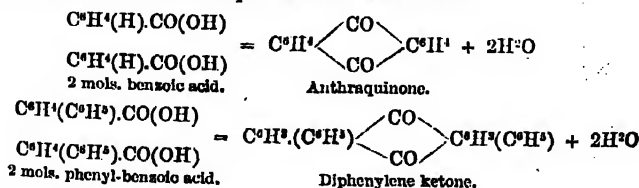
**DIPHENYL-BIURET.** See BIURET (p. 193).

**DIPHENYLENE KETONE**,  $C^{12}H^{10}O$ , is produced by heating diphenic acid with excess of quick-lime. It crystallises from alcohol in large, transparent, pale-yellow plates or thick compact crystals, melting at  $83.5^\circ$ – $84^\circ$  and boiling above  $300^\circ$ ; it volatilises slowly with vapour of water; dissolves in cold concentrated sulphuric acid with a wine-red colour; and is again precipitated by water, but only if the solution has not previously been heated. Diphenylene ketone introduced in small portions into fused caustic potash is converted into phenyl-benzoic acid  $C^6H^5(C^6H^5).CO^2H$ ; and on heating the calcium salt of this acid with quick lime, the ketone is regenerated, but at the same time a small quantity of diphenyl is produced, and a larger quantity of the latter may be obtained by heating the calcium salt without quick lime.

Regarding diphenylene ketone as  $C^{12}H^{10}O$ , its formation from diphenic acid is exactly analogous to that of dimethyl ketone (common acetone) from acetic acid:



Fittig & Ostermayer, however, who regard anthraquinone as a double ketone,  $C^{14}H^{10}O_2$ , think that diphenylene ketone may be better represented by the double formula  $C^{12}H^{10}O_2$ , in which case its formation from phenyl-benzoic acid will be analogous to that of anthraquinone from benzoic acid:

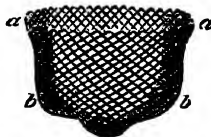
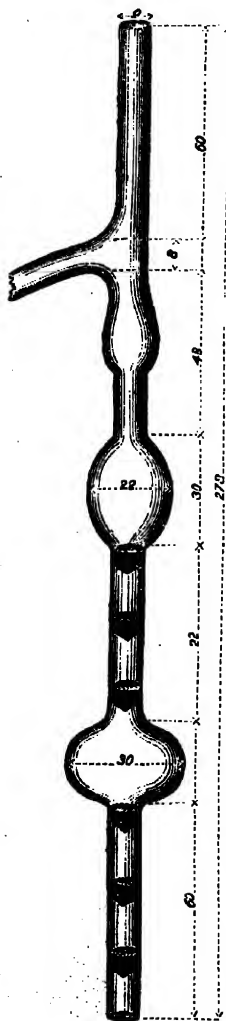


On this view, diphenylene-ketone is diphenyl-anthraquinone. When fused with potash, it again yields phenyl-benzoic acid, just as anthraquinone is resolved by the same reaction into two molecules of benzoic acid (see ANTHRAQUINONE, pp. 94, 95).

**DIPHENYLENE OXIDE**,  $C^{12}H^{10}O$ . This, according to Hoffmeister (*Zeitschr. f. Chem.* [2], vii. 24), is the composition of the supposed phenyl oxide,  $C^{12}H^{10}O$ , which Lesimple obtained (*Ann. Ch. Pharm.* cxxviii. 375), by distilling phenyl phos-

phate with excess of lime, and treating the oily distillate with potash. It crystallises from alcohol in fine colourless laminae having an aromatic odour, melting at 80°, and resolidifying at 51° (Lesimple). It is not attacked when its vapour is passed over red-hot zinc-filings. Heated to 220° in a sealed tube with phosphorus pentachloride, it is converted into a chlorinated body which crystallises from alcohol, and melts at 92° (Hoffmeister).

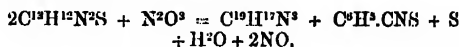
FIG. 14.



**DIPHENYL-METHANE.** See PHENYL-METHANES.

**DIPHENYLSULPHOCARBAMIDE, N<sup>2</sup>(CS)<sup>2</sup>** (C<sup>6</sup>H<sup>5</sup>)<sub>2</sub>N<sup>2</sup>. This compound, treated with a cold solution of nitrous ether in alcohol (obtained by saturating cooled absolute alcohol with nitrogen trioxide) is instantly

decomposed, evolving torrents of gas, which consists chiefly of nitric oxide and is free from carbon dioxide and oxysulphide. Some time after the termination of the experiment, the liquid, which is turbid at first, becomes perfectly clear, and a quantity of free sulphur is deposited, exactly equal to half the amount contained in the sulphocarbamido employed. The alcoholic liquid then contains phenylsulphocyanate and triphenylguanidine, nearly in the calculated proportion. The decomposition appears to be represented by the equation :



according to which the action of nitrous acid in alcoholic solution is perfectly analogous to that of iodine, chloride of sulphur, &c. (Claus, *Deut. Chem. Ges. Ber.* iv. 143).

**DIPHOSPHOCHLOROPLATINOUS ACID.** See PLATINUM COMPOUNDS.

**DIPHTHALIC ACID.** See PHTHALIC ACID.

**DIPROPYL.** See PROPYL.

**DISPERSION.** See LIGHT.

**DISSOCIATION.** See CHEMICAL ACTION (pp. 292-304).

**DISTILLATION.** Linnemann (*Ann. Ch. Pharm.* clx. 195) has contrived, for fractional distillation on the laboratory scale, an apparatus founded on the same principle as the so-called *Dephlegmators* used in distillation on the manufacturing scale, the vapour which rises from the boiling liquid being partially condensed in a tube interposed between the still and the condenser, so that the succeeding portions of vapour are forced to pass through this previously condensed liquid, whereby they undergo a kind of washing.

This is effected by fixing into the neck of the distillation flask a wide vertical glass tube (fig. 14), into which are inserted a number of thimble-shaped cups made of platinum gauze, the shape of which is shown at a b. The gauze of which these cups are made is formed of platinum wire about the thickness of a horse-hair, and the meshes are about  $\frac{3}{4}$  of a square millimeter in area. The cups are easily formed by stamping square pieces of this wire into a box-wood mould. To facilitate the condensation further, a bulb is blown on the tube after every two or three of the cups. The temperature of the vapour is measured by a thermometer inserted into the upper end of the tube, with its bulb in the uppermost enlargement. The lateral tube leads to the principal condenser.

The tube with six cups, represented in the figure at half its actual size, is used

for liquids boiling between  $150^{\circ}$  and  $180^{\circ}$ ; for those which boil between  $180^{\circ}$  and  $250^{\circ}$ , a shorter tube with two bulbs and five cups is used; and for those which boil below  $150^{\circ}$ , a larger one with three bulbs and eight cups.

As the distillation goes on, the liquid condenses in the cups and in the bulbs, faster than it can run back through the meshes of the gauze into the flask; consequently all the vapour has to pass through this condensed liquid, before it can pass off by the side tube into the condenser. To prevent too great an accumulation of liquid in the cups and bulbs, it is necessary to remove the flame now and then, and sometimes even to cool the upper part of the tube by blowing on it.

The advantages attributed to this apparatus are twofold: 1. It brings the purification of organic liquids by fractional distillation to a degree of perfection hitherto unattained. 2. It gives great exactness to determinations of boiling point, partly because it ensures the purity of the distilled liquids; and partly because the cooling influence of the masses of metal interposed between the boiling liquid and the thermometer prevents the so-called over-heating of the vapour, which is apt to take place with the apparatus commonly employed.

To ensure the purity of a liquid distilled with this apparatus, the several fractions are to be weighed, in order to find the principal fraction, and this latter is to be regarded as pure only when the loss which it suffers by repeated distillation does not exceed the average loss which occurs in the process, and when, after all parts of the apparatus and the bulb of the thermometer have been thoroughly heated, and the mercury has attained a constant height, it remains at that height till the last drop of liquid has distilled over, and falls as soon as the quantity of vapour left in the distillation vessel is no longer sufficient to yield any liquid distillate.

As an example of the use of the apparatus, Linnemann describes the purification of ethyl iodide, prepared in the ordinary way by the action of iodine and phosphorus on alcohol, washed with potash-solution and with water, then distilled with water, and dehydrated by phosphoric anhydride. The crude iodide thus obtained—yielded, after repeated distillation of the secondary fractions, and preservation of the fractions boiling: below  $70.9^{\circ}$ ; between  $70.9^{\circ}$  and  $71.9^{\circ}$ ; between  $71.9^{\circ}$  and  $72.5^{\circ}$ ; between  $72.5^{\circ}$  and  $72.9^{\circ}$ ; and between  $72.9^{\circ}$  and  $74^{\circ}$ ,—the twice distilled principal fraction  $70.9^{\circ}$  to  $71.9^{\circ}$  amounting to 570 grams. The further progress of the distillation is shown in the following table:—

*Fractional Distillation of Ethyl Iodide.*

	Weight of the Fractions in Grams.							Total	Loss
	a. to $71.0^{\circ}$	b. $71.0^{\circ}$ – $71.8^{\circ}$	c. $71.8^{\circ}$ – $71.9^{\circ}$	d. $71.9^{\circ}$ – $72.1^{\circ}$	e. $72.1^{\circ}$ – $72.3^{\circ}$	f. $72.3^{\circ}$ – $72.5^{\circ}$	g. Residue		
Fraction $70.9^{\circ}$ – $71.9^{\circ}$ , 570 grams distilled once	5	21	39	309	94	90	5	563	7
f distilled once	5	21	44	379	100	13		562	1
e once	5	24	47	460		22		558	4
d and e once	5	42	68	402		37		554	4
d once more	5	63	88	344		51		551	3
b and c dehy- drated with $P_2O_5$ and distilled twice.	56	27	14	384		59		540	11
e, f, g distilled once	56	27	14	417		10		533	7
				78 p.c.				Total 37 grams	

Hence it appears that 570 grams of ethyl iodide, originally boiling at  $70.9^{\circ}$  to  $71.9^{\circ}$  yielded, after twelve distillations, in which 37 grams were lost, chiefly by evaporation, 417 grams, or 78 p.c. of iodide boiling between  $71.9^{\circ}$  and  $72.1^{\circ}$ . On again distilling this quantity, after further dehydration with phosphoric anhydride, only 8 grams went over at  $71.9^{\circ}$ , but 393 grams between  $71.9^{\circ}$  and  $72.1^{\circ}$ ; and of this quantity

360 grams passed over at  $72^{\circ}$ . This point may therefore be regarded as the directly observed boiling point of the ethyl iodide. This observation was made under a barometric pressure of 730 mm.; and, by reducing this to the pressure of  $760^{\circ}$ , and making the necessary correction for the temperature of the portion of the mercurial column which projected above the condensing tube (for the details of which the original paper must be consulted), Linnemann calculates that the true boiling point of ethyl iodide is  $72.38^{\circ}$ .

For determinations, by this method, of the boiling points of homologous organic compounds, see p. 203.

On the Theory of Fractional Distillation, see Wanklyn (*Phil. Mag.* [4], xiv. 129); also J. C. Glashan, *ibid.* 373.

Pierre a. Puchot (*Compt. rend.* lxxiii. 443, 599) have made experiments on the distillation of mixtures of liquids insoluble one in the other. In this case the temperature of ebullition and the relative quantities of the two liquids in the distillate remain nearly constant. In the distillation of a mixture of water and amyl valerate, the temperature of ebullition was found to remain constant at  $100^{\circ}$ , and 13 volumes of water distilled over constantly to 7 volumes of amyl valerate.

In the distillation of a mixture of amyl alcohol and water, ebullition commences at  $96^{\circ}$ , and remains nearly constant at this point for a considerable time. Moreover, so long as the temperature remains constant, the volumes of water and of amyl alcohol condensed during any given time are invariably in a constant ratio, viz. 2 to 3; and the temperature does not begin to rise until either the water or the alcohol has wholly distilled over, leaving a surplus of alcohol or of water (as the case may be) in the retort. If the water was originally more than two-thirds of the volume of the alcohol, the temperature rises to  $100^{\circ}$  as soon as the whole of the alcohol has distilled over; but if less than the two-thirds of water was originally present, the boiling point rises to  $130^{\circ}$  as soon as the whole of the water has distilled over, the residue consisting wholly of amyl alcohol.

Butyl alcohol [of fermentation] gives similar results, the volumetric ratio in this case being 1 of water to 5 of the alcohol. The mixture boils constantly at  $90.5^{\circ}$ , i.e.  $9.5^{\circ}$  below the boiling point of water, and  $17.5^{\circ}$  below that of isobutyl alcohol.

When a mixture of water, butyl alcohol, and amyl alcohol is distilled, the temperature of ebullition is not constant, but regularly rises, always, however, remaining between  $95^{\circ}$  and  $96^{\circ}$ , and being higher as the quantity of amyl alcohol present is larger. The relative volume of water which distils over also increases continually, being, however, always greater than  $\frac{1}{4}$ th of the total volume which passes over, and less than  $\frac{2}{3}$ th; i.e. between the relative numbers found with butyl alcohol and water, and with amyl alcohol and water.

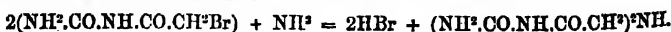
*Distillation of over-heated Liquids.*—Berthelot remarks that over-heated liquids not in the state of ebullition by no means cease to distil, but, on the contrary, often distil more rapidly than during ebullition. In distilling oil of turpentine, for example, under diminished pressure, the distillation might be advantageously accelerated by cautiously diminishing the pressure after the boiling has ceased. Many liquids behave in the same way when heated in open vessels; thus ethyl bromide, which ordinarily boils at  $38.5^{\circ}$ , may be heated to  $51^{\circ}$  without entering into ebullition. A liquid in such a state may be brought by agitation into sudden explosive ebullition, the temperature falling at the same time. Drops of such liquids often float about on the surface (*Bull. Soc. Chim.* [2], xiii. 315).

#### **DISULPHAMMONATES. DISULPHYDRATES.**

See SULPHAZOTIC ACIDS.

#### **DIURAMIDES** (E. Mulder, *Dent. Chem. Ges. Ber.* v. 1011).

*Diglycollamic Diuramide*  $(\text{NH}^2.\text{CO}.\text{NH}.\text{CO}.\text{CH}^2)^2\text{NH}$ , is produced, together with other products (apparently amidacetyl urea and hydantoin) by the action of ammonia on bromacetyl urea at the heat of the water bath:



When the solid substance which separates out on cooling is recrystallised from water, dissolved in hydrochloric acid, precipitated by ammonia, redissolved in hydrochloric acid, and treated with platinic chloride, a platinochloride is obtained in needles or prisms having the composition  $2[(\text{NH}^2.\text{CO}.\text{NH}.\text{CO}.\text{CH}^2)^2\text{NH}.\text{HCl}].\text{PtCl}_6$ ; and this platinum salt, treated with sul-ammoniac, yields diglycollamic diuramide in the free state, as a colourless crystalline body, insoluble in alcohol and moderately soluble in hot water.

The residue left when the crude product of the preceding reaction is treated with hydrochloric acid yields, on recrystallisation from water, a compound which appears to be triglycollamic triuramide  $(\text{NH}^2.\text{CO}.\text{NH}.\text{CO}.\text{CH}^2)^3\text{N}$ .

**DIXYLIT COMPOUNDS.** See XYLIT COMPOUNDS.

**DOLERITE.** Peterson (*Jahrbuch f. Mineralogie*, 1869, 36) and Sandberger (*ibid.* 1870, 205) regard dolerite and anamesite as merely structural varieties of the same rock-formation, and separate basalt from them as a chemically different rock. Sandberger regards, as a distinguishing character of the two former, the sparing occurrence, or total absence, of magnetic iron ore, and its replacement by hexagonal titanite iron ore.

H. Mohl (*ibid.* 1871, 885) has analysed the dolerite and tachylite of the Sababerg in Hesse, a basaltic mountain overlooking the sandy table land of the Reinhardswald between the Oberweser and the mouth of the Diemel, and consisting mainly of a true feldspathic dolerite, together with tachylitic and basaltic rocks. The dolerite (*a*) and tachylite (*b*) have the following composition:

	SiO <sup>2</sup>	TiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	MnO	CaO	MO	K <sup>2</sup> O	Na <sup>2</sup> O	P <sup>2</sup> O <sup>5</sup>	H <sup>2</sup> O
<i>a</i>	54.62	1.26	16.42	3.92	7.88	0.33	7.23	2.08	1.35	4.23	0.83	1.24 = 101.39
<i>b</i>	51.93	0.28	19.36	3.68	6.48	0.06	6.27	2.16	0.73	3.14	0.04	2.16 = 99.29

**DOLIUM.** The saliva of *Dolium Galea* contains in 100 parts by weight:

Sulphuric acid, free . . . . .	3.42	3.30
Sulphuric acid, combined . . . . .	0.20	0.15
Hydrochloric acid, combined . . . . .	0.58	0.60
Other substances, organic and inorganic . . . . .	1.08	2.35
Water . . . . .	94.00	93.60

A comparison of the weights of the animals with those of their shells and of the salivary glands, gave:

	I.	II.
Molluscs . . . . .	1305	520
Shells . . . . .	550	255
Glands . . . . .	850	80

(Pancieri and de Luca, *Sill. Am. J.* [2] xlix, 421).

**DOLOMITE.** This rock is commonly regarded—independently of necessary constituents amounting to 2 or 3 per cent.—as a double carbonate of magnesium and calcium having the same composition as bitterspar, viz.  $\text{CaCO}_3 \cdot \text{MgCO}_3$ . Korsten, who analysed 96 dolomites, concluded that in crystallised dolomites this proportion always holds good. According to other authorities, however, this is not always the case, and G. Bischof found that in dolomites whose composition only approximates to the formula above given, the magnesium carbonate is always below, and the calcium carbonate always above the calculated quantity. Experiment likewise shows that in non-crystallised dolomites, the two carbonates are present in very varying proportions, the calcium carbonate however always predominating. Rammelsberg, from a comparison of the published analyses of dolomites, deduces the three following formulae:

<i>a</i>	<i>b</i>	<i>c</i>
$\text{CaCO}_3 \cdot \text{MgCO}_3$	$3\text{CaCO}_3 \cdot 2\text{MgCO}_3$	$2\text{CaCO}_3 \cdot \text{MgCO}_3$
100 or 51.34	100 or 64.10	100 or 70.42
84 or 45.66	56 or 35.90	42 or 29.58
184	100.00	142
		100.00

He however points out distinctly that these simple stoichiometrical relations hold good only for the purer forms of dolomite.

The action of water containing carbonic acid on dolomites, differs according to their composition. Bischof's experiments show that from dolomites containing not more than 11 p.c. magnesium carbonate, carbonic acid water extracts only calcium carbonate, and hence it is probable that dolomites having the composition *b* or *c* would yield to carbonic acid water, chiefly calcium carbonate, and but little magnesium carbonate. From dolomites of the normal constitution *a* on the other hand, carbonic acid water takes up the whole without separation, and according to Bischof, deposits it again in the form of bitter spr. Hence he infers that dolomites containing druses of calc spar are imperfect dolomites, still in course of formation, whereas those which contain crystals of bitter spar are perfectly formed.

According to these results, the condition of a dolomitic formation may be inferred from the composition of the spring waters which issue from it, provided these waters have not previously passed through other strata from which they can take up any soluble ingredients. Such is the case with the dolomitic springs of that part of the Franconian Jurassic formation known as the Franconian Switzerland.

The valleys in this locality abound in springs, whereas the high table-lands are almost destitute of water, the rain which falls on them percolating quickly through the porous and fissured rocks, and issuing in the valleys in the form of springs.

The water of a considerable number of these springs has been analysed by Gorup-Besanez (*Ann. Ch. Pharm.* viii. Supplement-band 230). The only important constituents are calcium carbonate, magnesium carbonate, and silica, while chlorine, iron, alkalis, and bituminous organic matter occur only in minute quantities.

Many of these springs are pure dolomite waters, their percentage amounts of calcium and magnesium carbonates agreeing closely with those of dolomites occurring in the neighbourhood: these dolomites in fact, gave by analysis 57.32 and 57.21 p.c.  $\text{CaCO}_3$ , and 42.68, and 42.79  $\text{MgCO}_3$ , while the mean of the water-analyses gave 58.71  $\text{CaCO}_3$ , and 41.29  $\text{MgCO}_3$ . Some of the waters, however, differed widely from these numbers, containing as much as 88 or 89 p.c.  $\text{CaCO}_3$  to 12 or 11  $\text{MgCO}_3$ , and in the case of two other springs, 70 and 68 p.c.  $\text{CaCO}_3$  to 30 and 32  $\text{MgCO}_3$ .

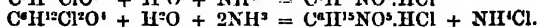
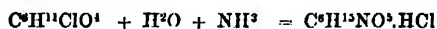
The occurrence of true dolomitic springs in the immediate neighbourhood of dolomite rock of normal composition, corroborates Bischof's view, that water containing carbonic acid dissolves true dolomites in fixed proportions, forming a solution from which by quick evaporation, a residue may be obtained, having the composition of the original dolomite. This is further corroborated by the experiments of Gorup-Besanez, on the amounts of calcium and magnesium carbonates taken up from dolomite by carbonated water in 5 to 8 and in 21 days.

From further experiments by the same chemist, it appears, however, that although carbonated water takes up from normal dolomites, fixed relative quantities of calcium and magnesium carbonates, the solution, when left to evaporate slowly, first deposits a large quantity of the calcium carbonate, while the magnesium carbonate is deposited only after long evaporation. Gorup-Besanez finds, moreover, that carbonated water takes up fixed relative quantities of the two carbonates from imperfect as well as from perfect dolomites, but that in no case is crystalline bitter-spar ever deposited from such a solution on evaporation. He therefore dissents from Bischof's conclusion, that a dolomite containing druses of bitter-spar is necessarily a perfectly formed dolomite.

The geological formation of dolomite is not yet completely understood, but the preceding facts seem to militate against Bischof's theory, that when magnesium limestone is subjected to the action of carbonated water, nothing but calcium carbonate is dissolved out till the molecular proportion  $1\text{CaCO}_3 : 1\text{MgCO}_3$ , belonging to true dolomite, is attained.

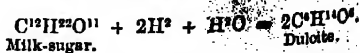
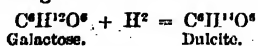
All the dolomites of the Franconian Jurassic formation are found by spectroscopic examination to contain lithium.

**DULCITAMINE**,  $\text{C}^6\text{H}^{13}\text{NO}^3$ . (G. Bouchardat *Compt. rend.* lxxiv. 1406). A base produced by heating 1 part of monoehlorhydric dulcitan  $\text{C}^6\text{H}^{11}\text{ClO}^4$  or of dichlorhydric (or dibromhydric) dulcite,  $\text{C}^6\text{H}^{12}\text{Cl}_2\text{O}^4$ , with 10 parts of alcoholic ammonia to  $100^\circ$  for six hours.



The dulcitamine hydrochloride may be dissolved out by absolute alcohol and precipitated in long needles by very gradual addition of ether. This salt is very soluble in alcohol or water, very slightly in ether-alcohol. The aqueous solution is neutral and has a faintly sweet taste. Treated with silver oxide, it yields free dulcitamine as a powerful base analogous to glyceramine, strongly blueing litmus, expelling ammonia from its combinations, absorbing carbon dioxide from the air, and forming by evaporation an uncrystallisable syrup, which gives with acids neutral salts crystallising with difficulty. The hydrochloride forms with platinum chloride orange-yellow needles of the salt  $2(\text{C}^6\text{H}^{13}\text{NO}^3.\text{HCl}).\text{PtCl}_4$ , very soluble in water and absolute alcohol, but not in ether, decomposed by heating, with a smell of burnt sugar and burnt horn. Auric chloride gives a difficultly crystallisable compound.

**DULCITE**,  $\text{C}^6\text{H}^{11}\text{O}^6 = (\text{C}^6\text{H}^9)^2(\text{OH})^2$  (Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 68; *Comp. rend.* lxxiii. 199; lxxiv. 665, 866, 1406; *Bull. Soc. Chim.* [2], xviii. 115). This saccharine substance, isomeric with mannite, is produced by the action of sodium amalgam on milk-sugar, on inverted milk-sugar, and on galactose, the glucose of milk-sugar:



An aqueous solution of galactose is acted upon by 2 p.c. sodium amalgam, the liquid being neutralised by dilute sulphuric acid from time to time; at the termination of the reaction, the liquid is exactly neutralised by acid, and the greater part of the sodium sulphate removed by crystallisation, the last portions by mixing the solution

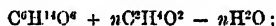


with twice its volume of strong alcohol. It is then filtered and concentrated to the consistence of a syrup. After some time small crystalline warty groups separate out, which may be removed and drained on filter-paper; a further quantity of crystals is deposited on leaving the liquid at rest. The substance thus obtained is readily purified by recrystallisation from water; on analysis it gave 39.3 and 39.1 p.c. of carbon, 7.85 and 7.9 p.c. of hydrogen, the theoretical numbers for dulcite being 39.5 p.c. carbon, and 7.7 p.c. hydrogen. The crystals are gritty between the teeth, but scarcely saccharine in taste; they are not fermentable in contact with beer-yeast; they melt at 187°, pure dulcite melting at 188.5°; they are very slightly soluble in strong alcohol; 100 parts of water at 21° dissolve 4.1 parts, pure dulcite dissolving to the extent of 3.6 to 3.7 parts, the difference being, doubtless, due to slight impurity. The solution of the artificially prepared substance has no appreciable action on polarised light. It is not browned on boiling with potash; neither does it reduce a cupro-potassic solution. Treated with dilute nitric acid, it yields crystals of mucic acid. All these characters show that the substance obtained by hydrogenation of galactose is identical with natural dulcite from the manna of Madagascar and from *Melanopyrum nemorosum*.

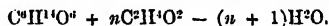
Milk-sugar, treated in like manner with sodium amalgam containing 4 p.c. sodium, likewise yields dulcite in monoclinic crystals, the angles of which agree exactly with those of the crystals of natural dulcite (ii. 349). The mother-liquors contain lactic acid. Inverted milk-sugar yields dulcite together with mannite, the latter crystallising in silky needles from the mother-liquors of the dulcite.

**Ethers of Dulcite.** 1. *Haloid Ethers*.—Dulcite dissolves easily in aqueous hydrochloric acid (saturated at 0°) with slight decrease of temperature, and the solution left to itself for 24 hours deposits bulky crystals of the hydrochloride,  $C^6H^{14}O^8$ ,  $HCl + 3H^2O$ . This compound is very unstable, and can exist only in an atmosphere saturated with hydrochloric acid; the crystals, when exposed to a current of air, give off the whole of their hydrochloric acid. The hydrobromide and hydriodide are similarly constituted, and somewhat more stable.

2. *Acetic Ethers*.—Dulcite submitted to the action of acetic acid produces a great number of neutral compounds, some of which are ethers of dulcite having the general formula—



while others are ethers of dulcitan,  $C^6H^{12}O^8$ , having the general formula—



*Diaceto-dulcite*,  $C^8H^{18}O^8 = (C^6H^{14})^1 \left\{ \begin{smallmatrix} (OC^2H^3O)^2 \\ (OH)^4 \end{smallmatrix} \right.$ .—Crystalline scales, fusible at 176°, volatile without residue on ignition; inodorous, insipid, slightly soluble in cold water, alcohol, or ether, soluble in lukewarm water; saponified by dilute alkalis.

*Diaceto-dulcitan*,  $C^8H^{16}O^7 = (C^6H^{12})^1 \left\{ \begin{smallmatrix} (OC^2H^3O)^2 \\ (OH)^2 \\ O \end{smallmatrix} \right.$ .—Volatile without residue on ignition; tastes very bitter; soluble in water, alcohol, and ether. At the ordinary temperature this substance is a colourless liquid, of the consistence of oil beginning to congeal.

*Hexaceto-dulcite*,  $C^{10}H^{20}O^{12} = (C^6H^{12})^1 (OC^2H^3O)^6$ .—Hard, friable, crystalline plates, fusible at 171°; sublimes at 200°–220° without alteration of its chemical composition. The sublimed product acquires for a time different properties, but gradually resumes its former state.

*Tetraceto-dulcitan*,  $C^{10}H^{20}O^9 = (C^6H^{12})^1 \left\{ \begin{smallmatrix} (OC^2H^3O)^4 \\ O \end{smallmatrix} \right.$ . Colourless and resinous in appearance; sublimes without residue; insupportably bitter; has a disagreeable odour when warm; nearly insoluble in water, soluble in alcohol and ether; saponified by alkali.

*Pentacetomonochlorhydro-dulcite*,  $C^{10}H^{19}ClO^{10} = (C^6H^{12})^1 \left\{ \begin{smallmatrix} (OC^2H^3O)^8 \\ Cl \end{smallmatrix} \right.$ , obtained by acting on dulcite with a mixture of acetic and hydrochloric acids, is an unstable compound, which, when heated in water, decomposes into pentaceto-dulcite, and hydrochloric acid.

*Pentaceto-dulcite*,  $C^{10}H^{20}O^{11} = (C^6H^{12})^1 \left\{ \begin{smallmatrix} (OC^2H^3O)^5 \\ OH \end{smallmatrix} \right.$ .—Crystalline body with properties very similar to those of hexaceto-dulcite, but less soluble in alcohol and ether. Heated for a long time to about 200°, it is partially transformed into pentaceto-dulcitan, with separation of water.

3. *Benzoic Ethers*.—*Hexabenzodulcite*,  $C^{18}H^{30}O^{12} = (C^6H^{12})^1 (OC^6H^5O)^6$ .—When

1 mol. dulcite is heated to 150° with 8 mols. benzoyl chloride containing benzoic acid, hydrochloric acid is evolved and the dulcite dissolves. The temperature is then raised to 200°; the excess of benzoyl chloride expelled by a current of carbonic anhydride; two volumes of alcohol added for one of the liquor, and the whole again heated. After some days small crystals are deposited, which, after another crystallisation from alcohol, consist of pure hexbenzodulcite. This body is solid and without taste or odour at ordinary temperatures. It melts at 147°, is quite insoluble in water or ether, and only slightly soluble in alcohol. When heated to 200° and suddenly cooled, it becomes amorphous, in which state it is much more soluble in alcohol, and even soluble in ether. After a few minutes, however, crystals are deposited from these solutions, having all the properties of ordinary hexbenzodulcite. Hexbenzodulcite is difficultly saponifiable. When it is treated with nitrosulphuric acid, the benzoic radical is attacked and hexnitrobenzodulcite is formed, which, when acted on by sodium-amalgam in presence of alcohol, furnishes dulcite and sodium amidobenzoate.

*Tetrabenzodulcitan*,  $C^{26}H^{20}O = (C^6H^5)_4 \left\{ \begin{matrix} (OC^7H^5O)^4 \\ O'' \end{matrix} \right\}$ .—When the mother-liquor obtained in the preparation of hexbenzodulcite is agitated with ether and sodium carbonate, and two volumes of alcohol are added to one of the liquor, a resinous precipitate is formed, which, after drying at 140°, has the composition of tetrabenzodulcitan. Like hexbenzodulcite, it is solid and without taste or smell at the ordinary temperature; is insoluble in water, and only slightly soluble in alcohol; but differs from that body in emitting, at 150°, an odour of benzoic ether, in volatilising without blackening, and in being very soluble in ether. It is saponified with difficulty. Nitrosulphuric acid apparently converts it into a nitrobenzodulcitan.

**DUPLOSULPHACETONE**,  $C^8H^{12}S^2$ . See SULPHACETONE (1st Suppl. 1047).

**DUST, VOLCANIC**. See VOLCANIC EMISSIONS.

**DURANGITE**. An orange-coloured mineral occurring with tinstone and topaz, near Durango in Mexico. It becomes transiently black when heated, and at a higher temperature yields a yellow glass and a scanty white sublimate, etching the glass at the same time; on charcoal it gives the reactions of arsenic with iron and manganese. It is partly decomposed by hydrochloric and nitric acids, completely by sulphuric acid, with evolution of hydrofluoric acid. The quantity of fluorine in the mineral is considerable, but could not be determined on account of the smallness of the quantity available for analysis. Hardness = 5. Sp. gr. = 3.95–4.03.

As <sup>2</sup> O <sup>3</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	MnO	Na <sup>2</sup> O	Si <sup>2</sup> O	F.
65.10	20.68	4.78	1.30	11.66	0.51	undetermined
55.22	20.09	5.06	1.28	11.86	0.70	„

The mineral consists, therefore, of an arsenate with a fluoride, corresponding with amblygonite among the phosphates. The degrees of oxidation of the iron and manganese are hypothetical (G. J. Brush, *Sill. Am. J.* [2], xlviii. 179). The crystals, according to measurements by J. M. Blake, are monoclinic, exhibiting the faces  $\infty P$ ,  $\pm 2P$ ,  $-P$ ,  $\infty P\infty$ ,  $4P\infty$ , and agreeing nearly in the magnitude of the angles and in type with yttritanite. Cleavage parallel to  $\infty P$  at an angle of 110° 10' (in yttritanite at 114°).

**DYNAMITE**. This name is applied to various mixtures of nitroglycerin with earthy substances. The original dynamite prepared by Nobel (*Dingl. pol. J.* xc. 124), consists of nitroglycerin mixed with  $\frac{1}{3}$  of its weight of porous silica (*infusorial silica*, *Kieselguhr*). It is said to exhibit the full power of the nitroglycerin contained in it, and to have the advantage, on account of its pasty consistence, of filling the bore-holes completely without overflowing, and to be less dangerous both in carriage and in manipulation.

The superior safety in the use of dynamite has been confirmed by the experiments of v. Wolfskron (*ibid.* excli. 174), and of Bolley, Pestalozzi and Kundt (*ibid.* excli. 140). The latter, however, recommend that dynamite should not be hermetically enclosed in metallic or other very solid receptacles, since it explodes when heated in a brass case tightly screwed or closed with a cork, also by a hard blow when placed between two metal plates. From 100 parts of dynamite, strong alcohol extracted 76.6 parts of nitroglycerin.

H. Schwarz (*ibid.* ccv. 429) found in two samples of explosives called dynamite the following materials:—

	No. 1, strong.	No. 2, weak, for coal-blasting.
Nitroglycerin . . . . .	67.5	58.9
Chalk and sawdust . . . . .	30.11	42.18
Moisture and loss . . . . .	2.39	0.97

Experiments on the relative explosibility of nitroglycerin and various kinds of dynamite have been made by Girard, Millat and Nogt (*Moniteur scientifique*, xlii, 58); on dynamite and its use in war by P. Champion (*ibid.* 91); and on the use of dynamite for breaking up large castings, by P. Champion (*Compt. rend.* lxxii, 770). See also *Chem. Soc. J.* [2] ix, 766-772.

**DYSLYTE.** See EULYTE.

## E.

**EARTHNUOT OIL.** This oil, expressed in the cold, contains about 4.5 p.c. of arachidic acid; that expressed with the aid of heat contains about 5 p.c. It is sometimes used to adulterate olive-oil, and its presence may be detected by separating out the arachidic acid. For this purpose the oil is saponified; the soap decomposed by hydrochloric acid; the resulting fatty acids converted into lead salts; the oleate of lead is removed by ether; and the remaining salts are again decomposed by hydrochloric acid. The fatty acids are then dissolved in alcohol of 90°, and the solution is left to cool. If earthenut oil be present, abundant crystals of arachidic acid will soon be seen to form. The crystals are washed with alcohol of 70°, in which they are perfectly insoluble, dissolved in boiling absolute alcohol, and the solution is evaporated to dryness and weighed. In reckoning the amount of arachidic acid obtained, allowance must be made for the quantity dissolved by the alcohol. 100 parts of 90 p.c. alcohol dissolve 0.25 of arachidic acid. The process does not succeed with a mixture containing less than 4 p.c. of earthenut oil, but with a 10 p.c. mixture the amount may be ascertained within 1 p.c. of the truth (A. Renard, *Compt. rend.* lxxiii, 1330).

**ECBOLINE.** See ERGOT.

**EGG.** On the nuclear structures of the yolk of the hen's egg, see NUCLEIN.

**ELLITE.** A hydrated cupric phosphate from Cornwall (see PHOSPHATES).

**ELDER OIL.** See OILS, VOLATILE.

**ELECAMPANE INULIN.** See INULIN.

**ELECTRICITY.** *Electromotive Force developed by the Contact of Metals, and the Modification of that Force by Heat* (Edlund, *Pogg. Ann.* cxxxvii, 474; cxi, 435; cxlii, 404, 534. *Phil. Mag.* [4] xxxviii, 263; xliii, 81, 213, 264).—It was observed by Peltier, in 1834, that when an electric current is passed through the point of contact of two different metals, that point becomes heated or cooled according as the direction of the current is opposed to or coincides with that which would be developed by the contact of the metals. The quantity of heat thus absorbed or developed has been shown by Edlund to be proportional to the product of the strength of the current into the electromotive power of the metallic couple, which may, therefore, be determined by measuring the quantity of heat absorbed or developed by a current of known strength.

With an apparatus constructed on this principle, for the description of which we must refer to Edlund's paper (*Pogg. Ann.* cxliii, 404, 534), the following results have been obtained:—

1. The electric tension series of the metals, as determined by electroscopic experiments by Volta, Péclet, and others, exhibits no immediate relation to the electromotive forces developed by the contact of the metals: consequently, the amount and nature of these forces cannot be determined from the electric tension series. It appears probable, also, that the electric tension depends, not entirely on the contact between the two metals, but also on the film of gas or water condensed on their surfaces.

2. The order of the metals in the electromotive series is the same as that in the thermo-electric series.

3. The electromotive force for the combinations of copper with iron, cadmium, zinc, silver, gold, lead, tin, aluminium, platinum, palladium, and bismuth, increases with the temperature when the experiments take place at a temperature not exceeding +30°.

4. The thermo-electric forces which, at a given difference of temperature, arise in different metallic combinations, are not proportional to the electromotive forces of these same metallic combinations.

5. If, with the aid of the second fundamental principle of the mechanical theory of

hent, we calculate the modifications undergone by the electromotive forces of contact in consequence of the increase of temperature, results are obtained which do not agree with experiment.

According to Crova (*Compt. rend.* lxxiii. 440) the electromotive power of voltaic batteries with two liquids varies with their temperatures, decreasing as the temperature rises in Daniell's arrangement, and increasing with the temperature in that of Grove, while, in one-liquid batteries like that of Smee, it is independent of the temperature. This is easily shown by arranging two galvanic couples of the same kind with their poles in opposite directions, and interposing a galvanometer in the circuit. On heating one of the couples, the needle will be deflected in a direction varying according to the nature of the arrangement.

*Electromotive Force of Platinum in Contact with various Liquids.*—

When two electrodes of non-platinised platinum have remained for a certain time in an acid liquid, dilute sulphuric acid for example, they, for the most part, do not give rise to any perceptible current; but if one of them be washed with distilled water and wiped with bibulous paper, it is found, on reimmersion in the acidulated liquid, to be strongly negative with regard to the one which has remained in the liquid. The electromotive force of the circuit quickly diminishes, but an hour generally elapses before it is reduced to nothing. If the acidulated water be replaced by potash solution, the electrode which is washed with water and dried with bibulous paper, becomes distinctly positive towards that which has remained in the alkaline liquid. With the alkaline solution either non-platinised or platinised electrodes may be used, and in the latter case the electromotive force is considerably stronger than in the former. When a platinised and a non-platinised platinum electrode are immersed in the same liquid, the former is always the positive element. These effects may, perhaps, be attributed to the formation, on the surface of the platinum, of compounds of that metal with the acid or alkaline constituents of the liquid, the formation and decomposition of these compounds requiring a considerable time. This view is supported by the fact that, if one of two similar platinum wires which give no current when placed in distilled water be immersed for a long time in dilute sulphuric acid, then quickly washed, dried between filter-paper, and again plunged into the distilled water, it will be distinctly negative towards the other. As all acids which have been examined give the same result as sulphuric acid, whereas all alkaline solutions produce the opposite effect, the experiment just described may be used to ascertain whether a liquid is acid or alkaline, even when, on account of its great dilution, it no longer exhibits any reaction with test-paper. In this manner it has been found that no solution is strictly neutral; the salts of the heavy metals exhibit a decided acid reaction, while those of the alkali-metals react more or less distinctly alkaline (Gaugain, *Compt. rend.* lxxix. 1300).

Subsequent experiments by Gaugain (*ibid.* lxx. 74) leave it undecided whether the unstable surface-modification of the platinum is due to superficial impregnation with distilled water, which then acts electrically towards the acid, or whether the action of the acid on the platinum produces on the surface a more electropositive compound, which is gradually destroyed on subsequent immersion in distilled water. The drying of the platinum at different temperatures gives rise to complications of the phenomena similar to those observed by Becquerel (p. 445).

If two plates of platinum, the surfaces of which have been polished with emery-paper, are allowed to remain in distilled water for 48 hours, no electric current is generated when the two plates are brought into metallic connection through a delicate galvanometer. If, however, one of the plates be taken from the liquid, and its surface rubbed with any soft substance, it is found, when plunged again into the distilled water, to be negative to the plate which has remained in the water. When the surface is rubbed with filter-paper, a force of 30 units is developed: during friction with linen moistened with water 40 units are developed; and if the plate be rubbed with wet linen for some time, and then with dry linen, the force rises to 56 units. The unit of force which serves as a measure is the electromotive force of a thermoelectric couple

$$\left( \begin{array}{c} \text{Bi} - \text{Cu} \\ 0^{\circ} - 100^{\circ} \end{array} \right).$$

The above values are given for the force developed when the plate is plunged into distilled water immediately after rubbing; if, however, the plate, after rubbing, be allowed to remain either in dry or in damp air for some time, the force generated on immersion gradually decreases. The current generated diminishes very quickly after the plate has been immersed for a short time; after 10 minutes it diminishes to about one-half, but it is some hours before the two plates become perfectly neutral to each other. The cause of these currents may be that after rubbing the plate does not immediately become thoroughly moistened by the water, so that if it be taken out of the water, the liquid on the surface will be seen to run together into drops. The plate, however, recovers its power of being thoroughly moistened if it be

heated in a spirit-lamp flame. It seems as if the rubbing caused a small film of grease to be deposited on the surface, which is destroyed by heat (Gauguin, *Compt. rend.* lxxiv. 610).

*Development of Electricity by Contact of Metals, Charcoal, &c. with Water, Acids and Saline Solutions* (Becquerel, *Compt. rend.* lxx. 481).—1. The contact of a neutral saturated solution of potassium sulphate with a similar solution of potassium nitrate, produces, with two platinum plates, an electro-motive force = 3.4, and with two gold plates, a force = 2 (that of a Grove's element = 100).

2. Circuits formed of pure gold plates, and of gold plates alloyed with 0.1, 0.2 and 0.5 copper, in distilled water gave the values 5.6, 7.5 and 11.2. The electromotive power increases therefore with the proportion of copper; the pure gold is less attacked than its alloys.

3. Gold and its alloys were always positive\* towards platinum, and gave the electromotive forces 2.8, 4.50, 6.8 and 7.5.

4. Gold and its alloys were also positive to nearly pure graphite, giving the electromotive forces 5.6, 8.7, 12 and 14.

5. Platinum is negative to palladium and iridium.

6. Graphite containing traces of iron is positive to pure graphite. The latter body is less attacked by water than any other.

The other bodies examined by Becquerel are divided into three classes: (1) charcoal is usually positive when plunged into distilled water (kept in platinum vessels to ensure the absence of soda). (2) Gold, platinum, palladium and iridium are sometimes negative. (3) Silver and the base metals, after being moderately heated, are always negative. The positive excitement of charcoal is due to the fact that after it has absorbed air, it slowly produces carbonic acid, this chemical action rendering the charcoal positive, and the water negative. This property may be intensified by strong ignition. The action of distilled water on the non-oxidable metals is intimately related to their capability of absorbing gases, especially hydrogen and oxygen, on their surface, and giving them up again at higher temperatures. The predominance of one or the other gas determines the positive or negative excitation.

The following experiments relate to the polarising property of platinum:—

A platinum wire enclosed in a tube and heated on the sand-bath, becomes after heating:

For a few minutes . . . . .	positive to water.
For half-an-hour . . . . .	negative "
To a little below a red heat . . . . .	positive "
To a white heat . . . . .	negative "

Heated for a few seconds in boiling distilled water, it loses nearly all its polarisation. These effects can only be explained by supposing: 1. That the aqueous vapour in the atmosphere is decomposed under the influence of the metal, at a more or less elevated temperature. 2. That a difference in the mode of absorption of the hydrogen and oxygen takes place, according to the time for which the heating is prolonged. When perfectly depolarised, neither platinum nor gold gives a current with water. The negative excitation of silver and the oxidable metals after moderate heating, arises from their becoming covered with a thin film of oxides, which protects them from the further action of the water, whereas a perfectly clean surface is attacked, and thereby becomes positive. This effect is analogous to the passivity of iron immersed in nitric acids. Many non-metallic bodies, as white quartz and white topaz, possess the same property as the non-oxidisable metals of absorbing gases, especially hydrogen, and becoming positive after heating.

*Contact of Metals with Acids, &c.*—When the free ends of two wires of gold or platinum connected with the polar wires of a galvanometer, are dipped into strong nitric acid, and one of them withdrawn, heated in a lamp-flame to free it from adhering liquid, and then immersed again, this wire becomes successively positive, negative, positive. The first effect is probably due to capillary affinity; the second to the polarisation of the two wires by the incipient current, and the decomposition of the solution; the third to a second polarisation. If the acid is dilute, the wire remains positive for a few seconds, in consequence of absorbing hydrogen liberated by the decomposition of the water induced by heating. With hydrochloric acid, sulphuric acid, ammonia and neutral saline solutions, such as sodium chloride or sulphate, barium chloride, potassium nitrate, &c., the platinum becomes negative in consequence of the air absorbed during cooling, which in contact with the liquid acquires negative electricity.

\* The terms positive and negative are used in Becquerel's memoir, with reference to the direction of the current in the portion of the circuit external to the battery, that is to say in the sense opposite to that which is usually assigned to them (ll. 416). In the account of his experiments here given, the usual meaning of the terms has been retained, that is to say, the more active metal is called positive.

According to Skeay (*Chem. News*, xxiii. 221) electric currents of considerable intensity are developed by either gold or platinum under the following circumstances:—

Two plates of gold (prepared chemically pure) are taken; one is placed in a cell partly filled with sea-water, and the other in a porous cell containing ammonium sulphide, or sea-water charged with hydrogen sulphide. On making connection, a small current passes from the gold plate in the inner cell to that in the outer, the electric currents obtained in this way being able to decompose solutions of gold, silver, and copper.

To avoid the electromotive action described by Becquerel, the solutions must be previously boiled to expel the air from them, and the plates of gold or platinum immersed, while red hot, in the solutions.

When potash or ammonia is substituted for ammonium sulphide, the currents obtained are very much weaker.

*Electromotive Power of Metallic Sulphides.* (W. Skeay, *Chem. News*, xxiii. 255, 291).—Those sulphides which have the power of conducting are also capable of generating electricity. A mass of iron pyrites and another of galena immersed in sea-water and connected by copper-wires with a decomposing cell of cupric sulphate, deposited the metal in a coherent form. The relative polarity of other sulphides is given in the following list, which is so arranged that each body is positive to all that succeed it:

Ferrous sulphide.	Cupric ferro-sulphide (copper pyrites).
Manganous sulphide (manganese blende).	Ferrie disulphide (cubical pyrites).
Zinc sulphide (zinc blende).	Antimonious sulphide (stibnite).
Stannic sulphide.	Auric sulphide.
Mercurous sulphide.	Platinic sulphide.
Argentie sulphide (artificial).	Ferrous arseno-sulphide (mispickel).
Lead sulphide (galena).	Carbon (graphite) sulphurised.
Cuprous sulphide (copper glance).	

Among the metals, zinc stands above ferrous sulphide, silver between silver sulphide and galena, platinum between platinic sulphide and mispickel, and carbon must be placed at the negative end of the series.

When a piece of massive galena is placed in voltaic contact with amalgamated zinc, and both are immersed in dilute sulphuric acid, in such a manner as to expose nearly the whole surface of the couple to the action of the acid, a galvanic current is at once established, gas is liberated at the surface of the galena, and the zinc is rapidly dissolved. If three or four such elements be connected together, a current is produced capable of decomposing acidulated water, and exhibiting all the effects of a small galvanic battery.

The galena which forms the negative element in these combinations may be replaced by other metallic sulphides, such as zinc blende, copper pyrites, ferrous sulphide, &c.: a difficulty, however, arises in establishing a current with iron pyrites, which may be overcome by completely immersing the couple in the acid for a short time; gas is immediately evolved at the point of contact, and the area of evolution rapidly spreads, until the whole surface of the specimen has become active. The gas liberated in a battery of this description is sulphuretted hydrogen, the nascent hydrogen exerting a desulphurising action upon the metallic sulphide, the ultimate effect of which is in some cases to completely reduce the mineral to the metallic state. These sulphides are also able to form among themselves a series of voltaic couples in presence of saline solutions, according as they differ from each other in respect to their affinities for oxygen. Thus, galena and copper pyrites produce a voltaic couple in which the galena is the negative element, but the functions of the galena are reversed when combined with silver sulphide, this latter mineral being decomposed with less facility.

The fact that several metallic sulphides are capable of performing the functions of the negative element of a galvanic couple, shows that these minerals are fairly good conductors of electricity, to an extent, indeed, not hitherto recognised. Moreover since dissimilar sulphides generally are capable of setting up a galvanic action, and inducing chemical decomposition among themselves, these phenomena may perhaps have some relation to the formation and decomposition of metalliferous lodes.

**Galvanic Batteries.** Favre (*Compt. rend.* lxxi. 214) has constructed a modification of Daniell's battery, in which the zinc plate is replaced by a plate of hydrogenised palladium. This battery acts just like the original zinc-copper combination, and exhibits in a very striking manner the chemical resemblance of hydrogen to the metals, the hydrogen constituting in fact the active element.

Zalowski (*Compt. rend.* lxx. 321) has constructed a circuit of three fluids, consisting

of two porous vessels placed one within the other, the inner one containing nitric acid and a plate of carbon, the outer one sulphuric acid, and the whole being enclosed in a vessel containing solution of sal-ammoniac and a zinc plate.

Nettleton (*Chem. News*, xxii. 228) replaces the platinum plates of Grove's battery by aluminium. He finds that two couples with aluminium plates, 4 inches long and  $1\frac{1}{4}$  inch wide, decompose water very quickly.

Figuiet (*J. Pharm.* [4] xi. 280) replaces the platinised platinum in Smee's battery by charcoal covered with platinum or silver. To produce the platinum deposit the plate of gas-rotort charcoal is painted with a moderately strong solution of platinum chloride and heated over a Bunsen's burner till the metal is reduced. The silver coating is obtained by painting the charcoal with a solution of silver nitrate, converting the nitrate into chloride by holding the plate over fuming hydrochloric acid and heating it till the silver chloride melts. The reduction to the metallic state takes place in the battery itself, being produced by the hydrogen evolved at the commencement of the action. With plates thus coated, the hydrogen all escapes in bubbles, without polarising the charcoal.

Still more economical is a coating of finely divided carbon, which may be produced by heating up the contents of an egg with five or six times its bulk of water and half its bulk of syrup, coating the charcoal with this mixture two or three times, drying it each time on the surface, and then heating it over a gas or alcohol flame till it no longer gives off smoke.

Plates thus prepared and well washed with water are said to give currents which remain constant for years; and the batteries, which are clean and easily managed, appear to be well adapted for applications in which large quantities of electricity are required, such as electrodeposition of metals, electric lighting, magneto-electric machines, &c.

H. Highton (*Chem. News*, xxiv. 142) describes some new galvanic combinations contrived chiefly with the view of removing the hydrogen and its products of combination from the surface of the negative plate. This may be effected in all known batteries by heating the liquid from below, so that the bubbles of vapour thereby liberated may carry the hydrogen with them. Every form of battery is said to be greatly increased in power by this expedient. In Daniell's battery Highton proposes to surround the zinc with a solution of a neutral sodium salt and sodium silicate, or better, to use magnesium as the positive plate, and surround it with a solution of nitrate and silicate of sodium; this combination is rather costly, but affords a very strong and constant current. A very complete and not too costly oxidation of the hydrogen evolved on the carbon plate may be effected by surrounding this plate with sodium permanganate; the supply of this salt must, however, be continually renewed if a constant current is to be kept up.

The best and cheapest oxidising agent, however, is said to be atmospheric air. To render it available in this way, the negative plate of platinum or charcoal is placed in a deep earthenware cell, and packed in ash or similar porous material, which is wetted, but not filled, with nitric acid. A moist porous envelope is thus obtained, in which the deoxidised substances find sufficient atmospheric oxygen [and nitric acid vapour] to reoxidise them.

S. O. Sharples (*Sill. Am. J.* [3] i. 247) has examined a number of liquids with regard to their use in galvanic combinations. The following arrangement was found to give a constant current for 12 hours, without the inconvenience of acid fumes. The outer space round the hollow zinc cylinder of an ordinary Bunsen's cell is filled with sulphuric acid of sp. gr. 1.84, mixed with 9 vol. water. It is recommended to leave the acid thus diluted to stand for some time till all the lead sulphate has settled down, and make use of the clear liquid. To fill the porous cell containing the carbon cylinder, commercial nitric acid is saturated in a warm place with potassium bicarbonate, and mixed with a third of its volume of sulphuric acid, after which a quantity of water is added sufficient to redissolve the precipitated chromic acid. The addition of the sulphuric acid gives to the last-named mixture a greater conducting power, and renders it less costly. The electromotive force of this combination is equal to that of a Bunsen's element, and the internal resistance one-half that of the latter.

The replacement of the inner liquid by a solution of chromic acid in nitric acid, suggested by W. Gibbs, was found also to give a constant current, having an electromotive force equal to 1.2 that of a Bunsen's element; the internal resistance was the same. The high price of chromic acid, however, is an obstacle to the general use of this combination.

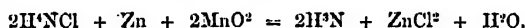
A combination consisting of zinc and charcoal in a solution of chromic acid in dilute sulphuric acid, devised by Bunsen, is described by Roscoe in the *Reports of the British Association* (1870, p. 47). Its electromotive power is there said to be that of a Grove's element as 25 : 18. Sharples found it to be twice that of a Daniell's

and 1·2 that of an ordinary Bunsen's element; but the current was not constant and the zinc was strongly attacked by the chromic acid. The use of manganese dioxide and nitric acid in the porous cell of Bunsen's battery gave feeble results, the strength of the current being = 1·43 of a Daniell's element. The current was variable, and nitrous fumes were evolved.

J. H. Koosen (*Pogg. Ann.* cxliv. 627) replaces the nitric acid in Grove's battery by a solution of potassium permanganate mixed with  $\frac{1}{30}$ th sulphuric acid; this combination raises the electromotive force from 1·6 to 2·0 Daniell. To render the current constant an addition of  $\frac{1}{30}$ th to  $\frac{1}{15}$ th of strong sulphuric acid is necessary. This acid decomposes the permanganate into oxygen which passes over to the zinc, potash which remains dissolved in the liquid as sulphate, and manganic hydrate which gradually settles to the bottom as a black powder. As an atom of potash is set free for each atom of zinc galvanically dissolved, the quantity of sulphuric acid consumed is double of that in any other battery; hence the large excess of sulphuric acid required. The use of charcoal instead of platinum in this form of battery, is not found advantageous.

*Laclanché's Battery.*—This zinc-carbon battery, in which the porous cell containing the gas-coke cylinder is filled up with a mixture of coarsely pounded manganese dioxide and gas-coke, and the exciting liquid is a solution of sal-ammoniac (*1st Suppl.* 555) has, according to J. Müller (*Pogg. Ann.* cxl. 308), an electromotive force equal to 0·896 of that of a Daniell's element, whereas Laclanché himself estimates it at 1·38. The difference between the two estimations is probably due, at least in part, to differences in the degrees of polarisation of the elements experimented on; this polarisation, according to Müller's experiments, being only partially removed by the manganese peroxide. In fact, this oxide, by giving up part of its oxygen to oxidise the electrolytically separated hydrogen, becomes inactive after prolonged use.

The loss of power in this battery is also partly due to the formation of a crystalline compound of ammonia and zinc chloride,  $(\text{NH}_4)_2\text{ZnCl}_4$ , which is deposited in the cells and on the zinc-plate, and obstructs the action. The formation of this compound arises from the liberation of ammonia by the action of the manganese dioxide on the sal-ammoniac:

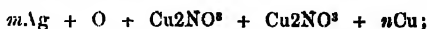


The ammonia is at first set free, and combines slowly with the zinc chloride when the two are present in the liquid in considerable quantity. The frequent addition of hydrochloric acid to neutralise the ammonia prevents the formation of the crystalline compound, and to a great extent the diminution of power of the battery (*Priwoznik, Pogg. Ann.* cxlii. 467).

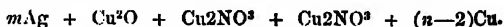
*Air-Battery* (Gladstone n. Tribe, *Proc. Roy. Soc.* xx. 290; xxi. 247).—When pieces of silver and copper, touching or connected by a wire, are immersed in an aerated solution of pure copper nitrate, a decomposition of the salt ensues, accompanied by a deposition of cuprous oxide on the silver, with a corresponding dissolution of the copper, and a flow of electricity through the liquid from the positive to the negative metal.

The reaction may be represented by the following formulæ:—

Before contact:



After contact:



This decomposition takes place only when the oxygenised solution of copper nitrate is in contact with the silver, and it is independent of any action of free oxygen on the copper; and if free oxygen can be supplied to the solution at the same rate as it combines to form cuprous oxide, the action will go on at about the same rate as long as any metallic copper remains.

To facilitate this as much as possible, the silver plate is placed in a horizontal position just under the surface of the liquid in the cell, and, in fact, converted into a small silver tray full of crystals of the same metal, which rise in projections above the surface. The copper plate lies horizontally under it, separated, if necessary, by a piece of muslin, and connection is made by a wire. Holes are made in the silver tray to facilitate the movements of the salt in solution. The solution itself may be contained in a shallow trough or saucer, and the whole arrangement put upon a wooden stand, the plates being attached to two uprights fixed in the stand.

An increase in area of the silver plates causes almost a proportionate increase in the current. Heat greatly increases the activity of this combination, a cell giving a deflection of  $40^\circ$  at  $20^\circ$ , gave one of  $250^\circ$  at  $50^\circ$ ; and the increase in the higher degrees of this range of temperature was much greater in the lower. The strength of copper nitrate which gives about the maximum effect is 6 p.c.



From the nature of the reaction it might be expected that the current would gradually diminish, on account of the using up of the oxygen in the neighbourhood of the silver. Such a diminution always does take place at first, and consequently agitation of the liquid has the effect of increasing the action. On breaking contact for some time, so as to allow of the absorption of oxygen from the air, the current, upon again making contact, is as strong, or nearly so, as originally.

On placing a cell, with plates connected by a wire, under a bell-jar full of air over mercury, the mercury rose from absorption of oxygen, and the oxygen was so completely removed that a lighted taper was immediately extinguished in the remaining gas.

Comparative experiments with aerated and deaerated solution of copper nitrate showed that the amount of action in the latter case was small, a result clearly attributable to the difficulty of completely excluding air. Two experiments were made alike in all respects, except that in one case the cell used was filled with a solution simply deprived of oxygen, while the other cell was filled with a solution through which a current of carbonic anhydride had been passed for some time. The first was placed in the air, and gave a deflection of 110 rising to 115, but the second was placed in a vessel full of carbonic anhydride and gave a deflection of 20, which gradually fell to 3.

The cuprous oxide deposited on the silver is compensated by an equivalent dissolution of the copper-plate. The cuprous oxide is sometimes deposited in crystals visible to the naked eye, and shown by a lens to be regular octahedrons.

One cell having plates two inches in diameter was found sufficient to decompose such metallic salts as the nitrates of copper, silver, and lead, platinum being used for the negative electrode, and for the positive the same metal as existed in the salt experimented on. Six cells were sufficient to decompose dilute sulphuric acid, and dilute hydrochloric acid pretty quickly, copper electrodes being employed.

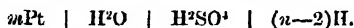
The theoretical interest of this battery lies in the fact that it differs from all other galvanic arrangements, inasmuch as the binary compound in solution is incapable of being decomposed either by the positive metal alone, or by the two metals in conjunction, without the presence of another body ready to combine with one of its elements when set free.

Grove's gas battery is essentially different from this, if the oxygen and hydrogen condensed on the platinum plates play the part of the two metals; but it closely resembles this battery, if hydrogen acts the part of the positive metal, and platinum that of the negative; the dilute sulphuric acid will then be decomposed on account of the simultaneous presence of the oxygen which can combine with the liberated hydrogen. Viewed in this manner, Grove's gas-battery is only a special case of the reaction above mentioned, and the formulæ will be:—

Before contact:



After contact:



**Electro-capillary action.** (Becquerel, *Compt. rend.* lxiv. 919, 1211; lxx. 51, 720, 752; lxxi. 77, 245, 766, 1066; lxxiii. 1285; lxxix. 1037; lxx. 68. *Jahresb. f. Chem.* 1867, 111.; 1868, 82; 1869, 155; 1870, 143).

When a tube closed at one end and having a crack in the direction of its length, is filled with a moderately strong solution of cupric nitrate, and placed within another tube containing an equally concentrated solution of sodium monosulphide, the inner and outer liquids being at the same level, no copper sulphide is formed, but after a short time, there is deposited within the crack, and on the adjacent inner surface of the tube, metallic copper of crystalline aspect, which gradually increases in quantity, widening the crack, and ultimately breaking the tube. With dilute solutions, the action is the same, but takes place more slowly.

To obtain capillary spaces of uniform width, two plates of glass or rock-crystal were laid one on the other, and held together by threads, or by means of ebonite provided with screws. When the plates were placed in the upright position, a small glass vessel, containing the liquid to be introduced into the capillary spaces, was cemented on to their upper ends. When they were to be placed horizontally, the upper plate, at least a centimeter thick, was perforated in the centre by a cylindrical hole of 4 or 5 mm. diameter for introducing the liquid. Sometimes also this aperture was surmounted by a glass tube several centimeters long, so that the column of liquid might exert a certain pressure on the liquid in the capillary space, which is especially necessary when the entrance of the liquid is rendered difficult by very close approximation of the plates. Sometimes also a strip of filter-paper is interposed between the plates, whereby the distribution of the liquid is rendered more uniform. The width of the

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capillary spaces, both of the cracked tubes and of the glass-plate apparatus, was very exactly determined by means of an apparatus devised by E. Becquerel for measuring the electric resistance of the liquids contained in them, this resistance being compared with that of the same liquid in a capillary tube of known diameter; by this means the width of a capillary space may be estimated down to a few thousandths of a millimeter.

By means of these apparatus, reductions may be effected of copper, silver, gold, nickel, lead and tin. The result appears to be due to the combined action of chemical affinity, molecular attraction and electricity. The two liquids acting on one another through the capillary space form a galvanic couple, the circuit being completed in the first instance by certain parts of the walls of that space, and afterwards by the separated metallic particles. The correctness of this view may be shown by dipping the ends of a bent copper-wire into the tube-apparatus above described, so as to form an ordinary galvanic circuit of two liquids and a metal. The end of the wire dipping into the alkaline solution is then attacked and forms the positive pole, while that which dips into the copper solution forms the negative pole, and becomes covered with metallic copper; at the same time thiosulphate and nitrate of sodium are formed, and the copper nitrate is decomposed, but no trace of metallic copper is formed, either on the crack or on the adjacent portions of the tube. As soon, however, as the wire is removed, the crack and the inner surface of the tube become covered with metallic copper. This shows that, in the absence of the wire, its conducting function is discharged by certain parts of the walls of the capillary space.

Effects similar to the above are also produced by placing the metallic solution in a tube closed at the bottom with parchment-paper, and immersing this tube in the solution of the alkaline sulphide. With this arrangement, metallic deposits are obtained on the inner surface of the tube, sometimes of the thickness of several millimeters; but the reactions are more violent than with the previously described arrangement, and the products alter more quickly. Ordinary paper and other porous bodies are altogether unfit for the production of this phenomenon. On the other hand, the separation of the liquids may be effected by means of a tube tied round at bottom, with linen, and filled to the height of 4 or 5 centimeters with pounded glass or quartz, fine sand or gypsum, the interstices of which form the capillary spaces.

By means of E. Becquerel's apparatus above mentioned, it was found that the reduction of most metals may be effected in capillary spaces, not exceeding a few hundredths of a millimeter in width; but when the width is reduced to a few thousandths of a millimeter, gold and silver are easily reduced, but other metals very slowly. The metallic precipitates formed in the plate apparatus, exert so strong a pressure, that if the bands do not burst, plates of 2 mm. thick are sometimes broken. This action may explain the splitting of rocks in which capillary actions take place in consequence of infiltration.

Metallic reductions likewise take place when the two solutions (the alkaline sulphide and the metallic salt) are separated by salt water, or by water acidulated with sulphuric or nitric acid; but if the alkaline sulphide or sulphhydrate be replaced by other liquids, as caustic potash or soda, or a solution of glycerin in caustic soda, or a concentrated solution of sodium chloride, the reduction either does not take place at all, or it is indistinct and not easily recognisable.

Electro-capillary actions may also be applied to the separation of silver or gold from copper, copper from iron, &c. A solution containing equal parts of silver nitrate and copper nitrate placed in a tube closed at bottom with parchment-paper, and immersed in solution of sodium sulphide, first yields metallic silver in dendrites or laminae, the copper not being reduced till after a considerable time. If a strip of paper saturated with a very strong acid solution of ferrous sulphate containing only a few thousandths of copper be placed between two glass plates, and the whole immersed in a solution of sodium sulphide, black ferrous sulphide is gradually deposited on the paper, and upon it an extremely thin film of metallic copper, which is then completely separated. The copper does not proceed from the paper, for the same results are obtained with asbestos. In like manner copper may be completely separated from a solution of chromous chloride, or from solutions of nickel or cobalt. From the latter, the nickel and cobalt may likewise be precipitated, and nickel separated from cobalt.

Electro-capillary phenomena are also produced when, instead of a strip of paper, a metallic plate covered with a moistened insoluble metallic compound is placed between two glass plates. When moistened iron pyrites is spread on a clean copper plate placed between two glass plates, and the edges cemented to prevent access of air, the iron sulphide is gradually decomposed, metallic iron is deposited here and there upon the copper, and copper sulphide is formed. In like manner with a zinc plate and recently prepared copper sulphide moistened with distilled water, zinc hydrate and

cuprous sulphide are deposited on the zinc plate in about a year, provided the water does not evaporate. With an iron plate and green cupric carbonate, crystallised ferric oxide is obtained and sometimes ferrous carbonate and metallic copper.

The preceding methods may also be applied to the preparation of various insoluble carbonates, aluminates, silicates, &c. in the crystallised state. When a tube closed at the bottom with parchment-paper, or with a double layer of Swedish filter-paper, and containing a moderately concentrated solution of calcium chloride, is immersed in a solution of sodium bicarbonate, the latter penetrates the paper, and forms rhombohedral crystals of calc spar. In like manner, aluminium silicate, lead chromate, barium sulphate, and barium carbonate may be obtained in the crystallised state.

In the following experiments, the alkaline solution was placed in the tube, and the metallic salt in the outer vessel. Concentrated solutions of potassium aluminate and chromic chloride yield on the surface of the diaphragm touching the alkaline solution (the positive surface) small hard nodules or laminae of aluminium monohydrate,  $Al_2O_3 \cdot H_2O$ , and on the opposite or negative surface green translucent laminae of chromic hydrate having a crystalline aspect. The aluminium hydrate appears under the polarising microscope to consist of double refracting prisms running out into pyramids. If the chromic chloride be replaced by hydrochloric acid diluted with an equal volume of water, the trihydrate  $Al_2O_3 \cdot 3H_2O$  is deposited on the positive surface in translucent crystalline crusts resembling diaspor. With cupric nitrate instead of chromic chloride, similar results are obtained in a short time, but the crystals of blue cupric hydrate often contain cupric silicate. These products are formed with peculiar facility when both solutions are concentrated, and there is no excess of acid on the one side or of alkali on the other. To obtain slow action, the tube must be closed with several layers of parchment-paper. With potassium aluminate and solutions of metallic salts, no reduction of metal takes place, the electromotive force being smaller than when an alkaline sulphide is used. Similar results are obtained with cupric nitrate, and a solution of zinc oxide or lead oxide in potash; also with solutions of antimonious chloride and potassium aluminate; the oxides separate in the crystalline state, the one dissolve in potash on the positive side, the one combine with acid on the negative side. With silicate instead of aluminate of potassium, there are deposited on the positive surface, very hard, transparent, single-refracting laminae of silicic hydrate, above this is formed a deposit of transparent gelatinous silica, which gradually acquires an opaline aspect, but becomes transparent again when immersed in water, and resembles hydrophtane.

By the simultaneous use of cupric nitrate, there is deposited on the negative side a hard blue crust, not however hard enough to scratch glass, from which by trituration and washing with a large quantity of water, crystalline fragments are obtained, having the form and composition of diopase. With a solution of free alkali, instead of an alkaline salt, crystallised cupric hydrate is deposited on the negative side. The reactions above described, alter as the diaphragm is more or less covered with deposits, and cease altogether when the crust has acquired a certain thickness.

If the same experiments are performed at a temperature of  $50^{\circ}$ – $80^{\circ}$ , the form of the deposits is somewhat different. If the negative plate of a battery of five Daniell's elements be dipped into the solution of potassium aluminate and the positive plate into that of chromic chloride, no precipitate is produced in the former, but in the latter chromic hydrate is deposited not only on the positive plate, but likewise on the diaphragm. On reversing the poles, no precipitate is formed in the chrome-solution, but aluminium hydrate is deposited in the alkaline solution.

If a solution of potassium carbonate be allowed to flow slowly on to a plate of gypsum placed between two glass plates, the surface of the gypsum gradually becomes covered with radiate groups of needles with truncated summits, having the physical and chemical characters of apophyllite, a double silicate of potassium and calcium.

If a tube closed with a double thickness of parchment-paper, and containing carbon sulphide, be immersed in a solution of potassium aluminate to such a depth that the two liquids stand at the same level, the alkaline solution gradually passes through the diaphragm, and forms, with the carbon sulphide, a sulphocarbonate, which floats on the surface of the latter, whilst the alumina is deposited as crystalline monohydrate on the diaphragm, and on the sides of the vessel. The same products are obtained when the diaphragm is omitted, and the one liquid is made to form a layer on the surface of the other.

The electromotive forces developed by two liquids separated by a capillary fissure, are usually very weak. Neutral solutions of potassium sulphate, ammonium sulphide, sodium chloride and sodium nitrate are negative in contact with distilled water. Sulphates give an evolution three times as strong as solutions of potassium nitrate or sodium chloride. The electromotive force varies with the concentration of the solution. If that of a nitric acid battery (Hansen's) = 100, that of a solution of caustic potash

of sp. gr. 1.215 in contact with water is 9.40; if the potash-solution be diluted with three times its bulk of water, the electromotive force will be reduced to 3.

The intensity of the electrochemical action in capillary spaces depends on the electromotive force, and the conducting power of the two liquids which are in capillary connection. The electromotive force is independent of the density of the liquids; but this is not the case with the chemical action, inasmuch as this action is in direct proportion to the conducting power of the circuit.

When nitric acid and solution of caustic potash are placed in the electro-capillary apparatus above described (p. 449), the nitric acid is decomposed, the oxygen, however, not separating at the positive side of the diaphragm, but apparently remaining in solution or combining with the potash to form potassium peroxide. If the potash be replaced by a solution of potassium plumbate, the electromotive force remains nearly the same ( $= 0.29$  of the zinc-carbon element); but the chemical actions change if a metallic solution, such as copper or silver nitrate, or gold chloride, be substituted for the nitric acid. The copper salt then yields, on the negative surface of the diaphragm, a thick deposit of anhydrous peroxide of copper. With a solution of silver nitrate or gold chloride, the metal is reduced, and peroxide of lead of considerable hardness is deposited on the positive side. Pure potash-solution is not capable of effecting a reduction of the metals on the opposite side of the capillary partition, the presence of an oxidisable body in the alkali being necessary to depolarise the positive side on which the oxygen collects, and prevent the development of the contrary current which interferes with the reduction (*Compt. rend.* lxxi. 197).

*Electro-capillary Actions in the Animal Organism.*—Bequerel has endeavoured to show that electrocapillary currents come into play in the conversion of arterial into venous blood, and in the accompanying chemical reactions. For the explanation of respiration and the nutrition of the tissue he sets out from the supposition that when two differently constituted liquids separated by a tissue with capillary pores, act on one another through the medium of these pores, the walls of which act as solid conductors, they give rise to electro-capillary currents, the direction of which is such, that the surface in contact with the liquid which plays the part of an acid forms the negative pole, the other the positive pole. These currents not only produce chemical combinations and decompositions, but likewise act as mechanical forces in transporting substances from one pole to the other (*Compt. rend.* lxxviii. 1285; lxxix. 1037).

Bequerel has also examined the electromotive force of the liquids which is contained in the bone-tissue of animals. When a platinum electrode is introduced into the marrow, and another applied to the surface of a bone of a freshly-killed animal, an electromotive force is exhibited about half as great as that of a Daniell's element. The liquid which penetrates all the pores and channels of the bones, develops, where it comes in contact with the liquid contents of the neighbouring tissues, an abundance of negative electricity, which, when platinum plates are introduced as above, unites with the positive electricity developed at the surface of the bone. When the metal plates are removed electro-capillary actions at once set in, the function of the conductor being then discharged by the solid substance of the bone. The current developed in muscular contraction, is attributed by Bequerel, in accordance with Dubois-Reymond, to the circumstance that the muscular juice in the interior becomes somewhat less alkaline during contraction than in the state of rest. The main result of the investigation is that the muscle-bone and nerve-currents have a purely chemical origin, and are not due to any peculiar electrical organisation of these tissues. In the functions of the muscles and nerves, electro-capillary currents play the principal part (*Compt. rend.* lxx. 68).

In the substance of the nerves and brain, a large number of currents are developed, in such a direction that the inner walls of the vessels and nerves exhibit reduction-phenomena, and their outer walls phenomena of oxidation. Between the grey substance of the brain which forms the outer, and the white substance which forms the inner part of the brain, there is produced a contact-current  $= \frac{1}{10}$  of the electromotive force of the nitric acid (zinc-carbon) element. The direction of the current is governed by the law above explained (*Bequerel, Compt. rend.* lxx. 345).

*Electro-capillary Actions in the Vegetable Organism.*—The development of electric currents in the interior of growing plants was observed several years ago by Bequerel (*Compt. rend.* xxxi. 40), and by Wartmann (*Arch. Phys. nat.* xv. 301), the strength of these currents increasing with the vigour of the plant, and the quantity of juice present in the several parts. Regarding these phenomena from the electro-capillary point of view, Bequerel now infers from his experiments that the pith and the cellular tissue in general are always positive at their contact with the other tissues. He finds, also, that the soil is always positive with regard to the roots, stem and leaves, i.e., to the liquids which moisten those organs or are contained in them. He considers that

the positive tissues, positive liquids, and the substances dissolved in the latter, are richer in oxygen than the rest (*Compt. rend.* lxxv. 752).

*Explanation of the preceding Phenomena without the aid of the Electro-capillary Hypothesis.*—O. Loew (*J. pr. Chem.* [2] iv. 271) is of opinion that the so-called electro-capillary phenomena may be explained without calling in the aid of electric currents, and proposes to designate the mode of action by the name *chemosmosis*.

When a moderate-sized crystal of cupric sulphate is immersed in a concentrated solution of potassium sulphide contained in a test-tube, the formation of a black crust of cupric sulphide is observed, and soon after a dark yellow coloration is seen to ascend from the crystals, indicating the formation of potassium disulphide. After twelve hours' standing, the black lump formed at the bottom, under the crust of cupric sulphide, is found to consist of metallic copper. Silver nitrate furnishes, under the same conditions, only a small quantity of metallic silver, whilst by far the greater part of the salt is not acted upon at all. Crystals of cupric sulphate covered with a concentrated solution of potassium hydrate yield a loose mixture of the black oxide and the hydrate of copper, and a blue solution of cupric oxide in potassium hydrate, whilst crystals of silver nitrate under the same conditions remain, as in the other case, unaltered below a thin crust of silver oxide.

Now as for every molecule of cupric sulphate a molecule of cupric sulphide is formed, whilst the water of crystallisation, having been solid before, passes into the liquid state, it follows that the crust of cupric sulphide must contain a great many more molecular gaps than that of silver sulphide, for this reason, that silver nitrate contains no water of crystallisation. A crust of sulphide once formed, the process of decomposition will go on in the same manner as before, only when the molecular gaps are large enough to allow of the passage of more molecules of potassium sulphide, whilst when the gaps are too small, chemosmotic decomposition, or electro-capillary phenomena, will be produced. The potassium unites with the group  $\text{SO}_4$ , metallic copper being separated, whilst the sulphur previously combined with the potassium remains outside the crust, forming potassium disulphide. The crust of silver sulphide, on the other hand, having no gaps, soon puts a more or less complete stop to the chemical action.

Loew is of the opinion that many of those chemical processes which take place in animal and vegetable organisms may be explained in a similar manner by supposing that the cellular membranes are provided with gaps, and possess a different molecular structure for each species of cells.

**Electrolysis. General Laws.**—G. Quincke (*Pogg. Ann.* cxliv. 1, 161) has developed a new theory of electrolysis, and of the conduction of electricity in liquids, based on the assumption that to each of the two component molecules which make up the entire molecule of an electrolyte, there is attached a certain quantity of free electricity, these quantities  $\epsilon$  and  $\epsilon'$ , which belong to the two component molecules, being either the same or different in sign and quantity. The separation of the component molecules arises from the different attraction which the several atoms composing the molecules exert on the two electric fluids.

The accelerating forces acting upon  $\epsilon$  and  $\epsilon'$  at a certain point are expressed by—

$$-\frac{dV}{dx} \epsilon \text{ and } -\frac{dV}{dx} \epsilon',$$

where  $V$  denotes the potential of the free electricity at this point and the force is reckoned as positive in the direction of the positive  $x$ . The charges  $\epsilon$  and  $\epsilon'$  carrying, as a rule, the particles to which they are attached along with them, soon attain, on account of the friction of the moving particles against one another, the constant velocities

$$v = -C \frac{dV}{dx} \epsilon, \text{ and } v' = -C' \frac{dV}{dx} \epsilon',$$

where  $C$  and  $C'$  are constants depending upon the quantity of mass to be moved, upon the friction between the particles, and upon the force with which  $\epsilon$  and  $\epsilon'$  are retained by the moving atoms. The force separating the ions is proportional to their mean relative velocity, and is expressed by

$$K = A(v - v') = -\frac{dV}{dx} (B\epsilon - B'\epsilon'),$$

where  $A$  and  $B = AC$  are constants.

If  $q$  represent the section of the electrolysed liquid,  $\lambda$  its conductivity, and  $i$  the current intensity, we get—

$$\frac{dV}{dx} = -\frac{i}{\lambda q}; \text{ and } K = \frac{i}{q} \frac{B\epsilon - B'\epsilon'}{\lambda};$$

from which it appears that the force tending to separate the constituents of an electrolyte is proportional to the density of the current, that is the strength of the current per unit of sectional area of the electrolyte. As long as this force is too small to overcome the chemical affinity, the liquid will behave as an insulator, but it may become conducting by an increase of the density of the current.

From these equations, the following general conclusions are deduced:—

1. The force tending to separate the ions increases with the electromotive force of the battery used, and is inversely proportional to the length, but independent of the section and of the conductivity of the liquid, supposing the resistance of the rest of the circuit to be negligible in comparison with that of the electrolyte.

2. The quantity of the ions separated is proportional to the mean relative velocity with which they pass one another.

3. According as the constituents of an electrolyte both approach to or recede from an electrode, or as they move with different velocities in opposite directions, the concentration of the liquid at this electrode will increase or decrease.

Quincke's formulae show further that the conducting power of a liquid increases with its temperature and condensation, and that, under certain circumstances, a maximum of conductivity may occur. They also show, in accordance with the results of experiment, that the quantities of different substances separated at the electrodes, and the ratios of these quantities when several chemical compounds contained in the same liquid are decomposed simultaneously, are independent of the density of the current. Further, that in a unit of time, different numbers of component molecules may pass through the same transverse section to the anode and cathode, these numbers being proportional to the density of the current and to a constant peculiar to each liquid, and therefore independent of the density of the current.

In most salts the passage of the electric current is attended with a decrease of concentration at both electrodes, whence it follows that the component molecules move in opposite directions, and  $\epsilon$  and  $\epsilon'$  have different signs. In solutions of  $\text{CdI}_2$ ,  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{ZnI}_2$ , however, Hittorff (*Pogg. Ann.* c. 542) observed concentration to take place at the anode, whence it follows that  $\epsilon$  and  $\epsilon'$  are in these cases both of negative sign.

*Conduction in Liquids without Electrolysis.*—The power of liquids to conduct electricity without at the same time undergoing decomposition being still somewhat doubted, though the experiments of Faraday and of Foucault afford strong arguments in favour of its existence, Favre (*Compt. rend.* lxxiii. 1463) has endeavoured to settle the question by experiments made under conditions in which electrolysis was impossible.

A Smee's battery of two cells which, so long as its two poles were unconnected, did not evolve a single bubble of gas, gave off, when its poles were connected through a voltmeter, 20 c.c. of hydrogen in 24 hours, showing that the circuit was complete, and therefore that conduction took place through the acidulated water in the voltmeter. No gas, however, was evolved from the voltmeter, whether the acid liquid contained in it had been previously saturated with the electrolytic gases, or had been previously boiled so as to expel dissolved gas. On replacing one of the Smee's elements by a Daniell's cell, a quantity of copper was deposited in the latter, equivalent to the gas given off by the Smee's cell, but no gas came from the voltmeter; and when solution of cupric sulphate was substituted as an electrolyte for the dilute sulphuric acid it was found that, after four days, though a deposit of copper had occurred in the Daniell's cell, the negative plate of the voltmeter did not exhibit a trace of it.

These facts indicate a true conduction in liquids distinct from electrolytic transference. In fact, according to previous experiments by Favre (p. 460), not less than three Smee's cells, whose voltaic energy is expressed by the number 15,000 per cell in units of heat for a certain amount of chemical decomposition, would be required to effect the electrolysis of the acid liquor of the voltmeter, in which, for a similar amount of decomposition, about 45,000 units of heat are required.

*Electrolysis of Water.*—Gladstone and Tribe (*Br. Assoc. Reports*, 1872, *Transactions of the Sections*, p. 75) find that pure water may be decomposed by zinc in conjunction with a more negative metal, the connection being made either within the liquid, or outside by a wire. With zinc and copper the effect increases slowly as the plates are approximated till they are within about an inch of each other, and on further diminishing the distance, the action increases at a rapidly accelerating rate. The decomposition is also accelerated by heat. With two plates  $1\frac{1}{2}$  inch distant from one another, the deflection of the galvanometer showed that the effect of raising the temperature from  $40^\circ$  to  $80^\circ$  was more than double of that between  $20^\circ$  and  $40^\circ$ . In an experiment with a 'copper-zinc couple,' that is to say, zinc-foil coated with finely divided copper by immersion in a dilute solution of copper sulphate, the following quantities of hydrogen were obtained:—

Mean temperature	Duration of experiment	Hydrogen collected	Hydrogen per hour
22.2	3 hours	3.1 c.c.	1.1 c.c.
31.4	2 "	11.1	5.5
55.0	45 minutes	10.4	13.0
74.1	15 "	15.5	62.0
93.0	10 "	20.1	74.6
	5 "	44.0	528.0

The last column shows the very great acceleration due to heat.

Five other experiments with the copper-zinc couple in which the gas was collected and measured at the end of every 24 or 48 hours yielded the following results:—

In experiment A, 33.4 grams of zinc-foil were employed, 2.6 meters long and 0.05 wide. The coils were kept apart by muslin. In experiment B there was used one meter of similar foil crumpled up. The two experiments continued almost *pari passu* for months, the amount of hydrogen gradually diminishing. Subjoined are the results of the first and last observations:—

	Mean temp.	Expt. A	Expt. B
Day	C°.	c.c.	c.c.
1	12.8	117.1	49.6
84	10.0	14.0	5.1

Under the microscope the bubbles of gas are seen to form, not on the zinc, but among the copper crystals, and sometimes to make their appearance on the glass at some distance off.

From the position of platinum in the electro-chemical series, it was anticipated that the effect would be still more marked with that metal in a spongy state on the zinc. The metal was deposited from the tetrachloride, and thoroughly washed. With 0.6 meter of foil the following quantities of hydrogen were obtained:—

Day	Mean temp.	Vol. in c.c.
	C°.	
1	11.7	113.6
8	7.7	12.3

Similar effects were obtained with water previously freed from air by boiling.

Iron and lead, similarly coated with copper, also decompose pure water, and the action of magnesium is greatly increased by conjunction with copper (*Proc. Roy. Soc.* xx, 218).

A metal less capable than zinc of decomposing water, likewise produces a deflection of the galvanometer if it be united with a metal still more negative. The order for pure water seems to be: platinum, silver, copper, iron, tin, lead, zinc, magnesium.

When the current of a single Daniell's cell is passed through pure water, the electrolysis is more easily effected between poles of a metal which has a considerable affinity for oxygen than between poles of a metal which has but little affinity for that element; with zinc poles, for example, the action is more than double of that between platinum poles of the same size and at the same distance. The order of efficiency for poles in the electrolysis of water seems to be: platinum, tin, silver, copper, iron, lead, zinc, magnesium. After a few minutes the power of tin was found to rise above that of copper. The other metals stand in the same order as in the previous list, where they are arranged according to the facility with which they produce electricity by their joint action on water.

Heating the liquid between the poles accelerates the action. With zinc poles the deflection increases about fourfold between 5° and 80°, and the action increases nearly *pari passu* with the temperature.

When the poles are formed of dissimilar metals, a current is established in the electrolytic cell which, according to its direction, either adds to or subtracts from the current originating in the Daniell's cell. Thus, if two poles of platinum be used, the effect with water is very minute; but if the negative platinum pole be replaced by one of zinc, pure water is decomposed by one cell of Daniell's battery with visible evolution of hydrogen. With poles of silver and zinc the following deflections were obtained:—

Positive	Negative	Deflection
Silver	Silver	27
Zinc	Silver	52
Silver	Zinc	7
Zinc	Zinc	33

When, therefore, the dissimilar metals were employed as poles, the decomposition of the water was not the mean of that producible by silver and by zinc, viz. 30, but 30 + 22 when the forces acted in the same direction, and 30 - 23 when they acted against one another (*Br. Assoc. Reports, loc. cit.*)

**Electrolysis of Alcoholic Iodides by the Copper-Zinc Couple.**—When zinc-foil coated with copper, as above, is heated to 100° with ethyl iodide, a decomposition takes place similar to that which is produced by zinc alone at higher temperatures, a small quantity of gas being given off, and ethiodide of zinc  $\text{Zn}(\text{C}^2\text{H}_5)\text{I}$  produced, which, when gently heated, is resolved into zinc iodide and zinc ethyl. When the couple acts on ethyl iodide in presence of water or alcohol, ethane  $\text{C}^2\text{H}_6$  is given off, and zinc iodohydrate  $\text{Zn}(\text{OH})\text{I}$  or iodethylate  $\text{Zn}(\text{OC}^2\text{H}_5)\text{I}$  remains behind.

The iodides of methyl, propyl, and amyl are decomposed in a similar manner (see the several ALCOHOL REACTIONS).

**Relations between Electricity and Heat.** F. Guthrie finds that the reaction between an electrified body and a neighbouring neutral body, whereby the electricity in the latter is inductively decomposed and attraction produced, undergoes a modification when the neutral body is considerably heated.

Under many circumstances the electrified body is rapidly and completely discharged, the action of discharge depending mainly upon the following conditions:—(1) the temperature of the discharging body, and its distance from the electrified one; (2) the nature (+ or -) of the latter's electricity.

With regard to (1) it is found that the discharging power of a hot body diminishes as its distance increases, and increases with its temperature, depending, however, not upon the quantity of heat radiated from the hot body to the electrified body, but chiefly upon its quality. Thus a white-hot platinum wire connected with the earth may exercise an indefinitely greater discharging power, at the same distance, than a large mass of iron at 100°, though the latter may impart more heat to the electrified body.

Neither the mere reception of heat, however intense, by the electrified body, unless the latter has such small capacity as to be itself intensely heated, discharges the electricity if the source of heat be distant; nor is discharge effected when the electrified body and a neighbouring cold one are surrounded by air through which intense heat is passing. But, for the discharge, it is necessary that heat of intensity pass to the electrified body from a neutral body, within inductive range.

White- and red-hot metallic neutral bodies exercise this discharging power even when isolated from the earth, but always with less facility than when earth-connected.

The hotter the discharging body, whether isolated or earth-connected, the more nearly alike do + and - electricities behave in being discharged; but at certain temperatures distinct differences are noticed. The - electricity, in all cases of difference, is discharged with greater facility than the +.

Various flames, both earth-connected and isolated, have an exceedingly great power of discharging both kinds of electricity.

The effects in regard to discharge are similar when platinum wire, rendered hot by a galvanic current, is used, and also when the condensed electricity of a Leyden jar is experimented on.

As hot iron shows a preferential power of discharging - over + electricity, so it is found that white-hot but isolated iron refuses to be charged either with + or - electricity. As the iron cools, it acquires first the power of receiving -, and afterwards of receiving +. Further, while white-hot iron in contact with an electrified body prevents that body from retaining a charge of either kind of electricity, as it cools it permits a + charge to be received, and subsequently a - one.

Many of these effects may, perhaps, be attributed to the existence of an electrical coercive force which, like the magnetic coercive of steel, is diminished by heat (*Phil. Mag.* [4] xvi. 257; *Proc. Roy. Soc.* xxi. 168).

**Thermic Equivalent of Electricity.**—F. Kiechl (*Wien. Acad. Ber.* lx. [2] 121), has re-determined the thermic equivalent of electricity, that is to say, the number of heat-units producible by the expenditure of a quantity of electricity capable of eliminating 1 gram of hydrogen at 0°C, and 760 mm. from water at 0°. This quantity of heat is the same as that which is developed by the combustion of 1 gram of hydrogen at 0°, and 760 mm. in oxygen under the condition that the resulting aqueous vapour is converted into water at 0°. The principle of the determination is as follows:—A voltmeter and a rheostat whose water-equivalent is exactly known, are enclosed in a calorimeter and traversed for equal times by a current of constant strength. When the voltmeter is placed in the circuit, the action is: evolution of N grams of detonating gas, and production of a quantity of heat Q; when the rheostat is inserted, the



effect is simply the production of another quantity of heat  $Q_1$ . The difference  $Q_1 - Q$  is therefore equivalent to the decomposition of  $N$  grams of water, or to the elimination of  $\frac{1}{2}$  N gram of hydrogen. The simplicity of the principle is somewhat disturbed by the polarisation of the electrodes, and by the circumstance that, under the most favourable circumstances, the evolved detonating gas leaves the calorimeter at the temperature of the latter, which is not exactly  $0^\circ$ , and under a pressure more or less different from 760 mm. Nine experiments gave, as the mean value of the thermic equivalent of electricity, as above defined, the number 33591. The experiments of Andrews on the direct combination of hydrogen with oxygen give 33808; those of Favre and Silbermann 34462.

*Thermo-electric Action of Liquids and Metals.*—Gore (Proc. Roy. Soc. xix, 324) has examined the relations of the temperature and chemical action of metals to their electrical state. Two shallow copper dishes connected by wires with a galvanometer, were so arranged in a U-shaped glass vessel with vase-like terminations, that the under surfaces of both could be placed in contact with any liquid contained in the glass vessel. One of the copper dishes was heated by pouring hot water into it, the other remaining at the temperature of the atmosphere. The general results are as follows:—The hot copper dish was *positive* to the cold one, when the active liquids were: hydrochloric, hydrocyanic, boric, and orthophosphoric acids; cupric chloride (weak solution); cobalt chloride; manganous chloride; chromic acid; chromic chloride; zinc sulphate (weak solution); magnesium sulphate; calcium chloride; strontium nitrate and chloride; barium chloride; sodium nitrate (strong solution); sodium chloride, iodide, carbonate, and diborate; sodium sulphate (strong solution); trisodic phosphate; potassium nitrate, chloride, and chlorate; potassium bromide (strong solution); potassium iodide (strong solution); potassium carbonate, hydrocarbonate and dichromate; ammonium hydrate and chloride; potassium cyanide and ferro-cyanide; zinc acetate; and sodium acetate. *Negative* in the following: nitric, chloric, hydrobromic, hydrofluosilicic, and sulphuric acids; ferrous sulphate; cupric chloride (strong solution); cupric sulphate; zinc sulphate (strong solution); sodium nitrate and iodide (weak solutions); potassium iodate; chrome alum; ammonium nitrate; oxalic, acetic, tartaric, and citric acids. In several instances where the hot metal was negative with a weak solution, it became positive in a strong one. The direction of the current appeared to be more influenced by the nature of the acid in a salt than by that of the base. The currents appear to be due either (1) to the direct influence of heat, the effect of which would be to make the hot copper negative in acid, and positive in alkaline liquids; (2) to chemical action, which sometimes overpowers the direct influence of heat and reverses the effect; or, (3) to both these influences combined. The action of air in promoting oxidation at the line where the liquid and metal come in contact with it, no doubt influences the amount of current, as also perhaps the direction. When the air-line is long, the metal becomes electro-negative in all cases, and gives stronger indications when the liquid has a powerful chemical action.

To ascertain whether the quantity of current was due to the difference in number of the molecules of liquid touching the hot and cold plates respectively, and also what amount of difference of strength of liquid was equivalent to the difference of temperature employed, experiments were made with liquids of unequal strength, instead of unequal temperature. The results show, that heat does not act simply by causing a greater number of molecules of each substance to touch the hot plate.

Following the suggestions of these researches, Gore has constructed a thermo-electric battery consisting of twelve bent glass tubes (fig. 15), closed at one end, and having a platinum wire sealed into that end, each tube being filled with a conducting liquid and having its outer end closed by a cork, in which was fixed a second platinum wire dipping into the liquid. The upper ends of the tubes are heated by hot water contained in an oblong tin box, having in its lower surface a long semi-cylindrical cavity to receive them. The tubes 1, 3, 5, 7, 9, 11 are filled with a dilute sulphuric acid, the alternate ones with aqueous solution of potash. The platinum wires are connected alternately at top and bottom, by means of binding screws, 1 and 2 at top, 2 and 3 at bottom, 3 and 4 at top, and so on. This battery produces a current very small in quantity, but of considerable intensity. By employing electrodes of larger surface, such as spirals of platinum, and more concentrated liquids, the quantity of the current might be considerably increased.

Gore has also shown that the currents produced by the friction of a liquid against

FIG. 15.



a polar plate rotating in its own plane, have no direct connection with those which are excited in the same liquids by heating; further, that the thermo-electric properties of liquids are not dependent on the molecular structure by virtue of which liquids, under the influence of magnetism, polarise light circularly.

**Noë's Thermo-electric Battery.**—In this battery the negative metal, an alloy similar to German silver, is drawn into wire; the positive alloy,\* which is very brittle and somewhat less fusible than antimony, is cast into cylinders. The metals are joined together by casting the cylinder round the thickened end of the wire, in such a manner that the wire is in the prolongation of the axis of the cylinder. Over the wire a short copper cylinder is passed, and pushed up against the positive metal, but it is prevented from coming in actual contact with it by the interposition of a piece of mica. Against these copper cylinders the flames of either gas or spirit lamps impinge, and are thereby prevented from fusing the positive alloy or burning through the wire. The elements are placed in double parallel series, which, in the larger batteries, are so mounted that they may be used in various combinations, either for quantity or intensity.

The electromotive power of one of these elements was found to be from 1.24 to 1.36 of the Jacobi-Siemens' unit, while the electromotive power of a Daniell's cell was found to be equal to 12 of these units. It requires, therefore, 9 to 10 Noë's elements to equal 1 Daniell. With larger batteries the electromotive power cannot, however, safely be raised above 1, otherwise superheating of parts is not to be avoided.

The larger battery examined consisted of 72 elements, which could be combined so as to form either, I. one series of 72 pairs, or II. one of 36 pairs, or, III. 18 of four pairs each. With each combination, the electromotive power, per element, was found to be one of the above units; the resistance of a single element was 0.05. A Bunsen's element, charged with concentrated nitric acid and with sulphuric acid of 1 in 10, has an electromotive power of 20, and with a good porous cell a resistance of about 0.3 in elements of the usual size. With a great external resistance, 20 of Noë's elements will therefore be equal to one of Bunsen's. With a small external resistance, 20 quadruple elements are somewhat stronger than one of Bunsen's. One Noë's element is about equal to 11 ordinary bismuth-antimony elements (temperature 0° and 100° C.). Even a single Noë's element produces considerable physiological effects when used with an induction apparatus.

The above-mentioned battery of 72 elements effects, with combination I. a copious decomposition of water; with combination II. it sets in action middle-sized Ruhmkorff's coils; and with combination III. and spirals of thick wire, it produces powerful electro-magnets.

In subsequent experiments it was found that the battery could be safely heated higher than was found expedient on the former series: it then gave a mean electromotive power of 1.14 per element, with a resistance of 0.054 (v. Waltenhofen, *Pogg. Ann.* cxliii. 113).

A new form of this battery has been devised by v. Waltenhofen, in which the negative wire fused to the positive metal is bent back from the point of contact at an acute angle. A small metallic rod is fused to the two elements at this same point. Twenty elements are arranged in a circle, the metallic rods just mentioned being in the centre. The space in the centre is covered with a plate of mica, and the metallic rods are then heated by means of a circular gas flame.

The electromotive power of twenty such elements is equal to 19.4, one Bunsen cell being equal to 20. If a Daniell cell be equal to 12, then one of these cells is about equal to 1. The resistance of each element = 0.056 (*Chem. Centr.* 1872, 530).

**Thermic Phenomena in the Voltaic Circuit.**—Favre (*Compt. rend.* lxxii. 369) has examined the heat-phenomena accompanying decompositions in the voltaic circuit, by means of an apparatus consisting of two mercury-calorimeters, one of which served to measure the internal work of a 5-pair battery (zinc, platinum, dilute sulphuric acid) enclosed within it, the other to measure the external work. Into this second calorimeter were successively introduced: (1) A sixth couple, identical with those of the first calorimeter; (2) a voltmeter consisting of a pair of platinum-plates of the same surface as the zinc-platinum pairs; (3) a voltmeter with two copper plates, likewise of the same surface, but immersed in a solution of cupric sulphate.

In the following table, A denotes the heat (in units or gram-degrees) taken up by the first calorimeter; B, the heat which is withdrawn from the battery, and represents its external work, also in gram-degrees, both reckoned for 1 equivalent of zinc (33) dissolved in the battery;  $\theta$ , the tangent of the angles of deflection of the galvanometer; C, the heat, also in gram-degrees, taken up by the voltmeter from the battery. The

\* The composition of these alloys is at present kept secret.

dilute sulphuric acid used in all the experiments contained in 1,000 cub. cent. 89.21 grams of sulphuric anhydride.

	A	B	$\delta$	C
1. Battery alone . . . . .	19,572	382	—	—
2. Battery with Galvanometer in the circuit . . . . .	18,474	1,480	3.1880	—
3. Battery, Galvanometer and sixth couple . . . . .	18,402	1,552	3.6069	—
4. Battery, Galvanometer and Voltmeter (platinum with dilute sulphuric acid) . . . . .	7,975	11,979	0.1095	59,895
5. Battery, Galvanometer, Voltmeter (platinum with nitric acid) . . . . .	8,888	11,066	0.0969	55,330
6. Battery, Galvanometer, Voltmeter (platinum with cupric sulphate) . . . . .	8,573	11,381	0.7623	56,905
7. Battery, Galvanometer, Voltmeter (platinum with cupric nitrate) . . . . .	8,424	11,530	0.8278	57,650
8. Battery, Galvanometer, Voltmeter (copper with cupric sulphate) . . . . .	11,091	5,863	1.8611	29,315
9. Battery, Galvanometer, Voltmeter (copper with cupric sulphate)*. . . . .	10,557	9,397	0.5658	46,985

\*Without the current, 1 eq. sulphuric acid (49) of the dilution above stated, and 1 eq. zinc (63) evolved 19,574 gram-degrees of heat; moreover, 1 eq. cupric sulphate, and 1 eq. zinc evolved 27,388 gram-degrees.

When a sixth couple is enclosed in the second calorimeter, the development of heat thereby is exactly one-fifth of that developed by the 5-pair battery in the first calorimeter, inasmuch as it proceeds exclusively from this one couple. When the second calorimeter contains the platinum voltameter, which evolves no heat, the entire quantity of heat proceeds from the battery, and the heat of the first calorimeter is diminished by a corresponding amount (*i.e.* by the fifth part of C). If the voltameter is fitted with copper plates, the heat developed within the second calorimeter proceeds partly from the battery, partly from the voltameter, the processes which take place separately in the zinc-platinum couple and the platinum voltameter here going on simultaneously (decomposition of cupric sulphate, with assumption of heat from the battery, and formation of an equivalent quantity of cupric sulphate with development of heat, which is added to that product by the current). Whereas therefore (in 3), the sixth couple in the second calorimeter develops 19.954 units of heat for each equivalent of sulphuric acid decomposed, the voltameter (in 4) consumes, for the same effect, 59,895 units which it abstracts from the current. Nearly the same values may be deduced from the decomposition of the copper salt in (6) and (7). After deduction of 7.975 heat-units (which Favre regards as required to overcome the resistance in the voltameter), there remain therefore 51,920 units, and these express the quantity of heat required for the decomposition of 49 grams of hydrogen sulphate (into  $\text{SO}^4$  and H, or, on the other hand, for the combination of  $\text{SO}^4$  with H).

The further consequences from the results obtained may be summarised as follows: The battery yields to the compounds which it decomposes, the quantity of heat required for their decomposition, and this quantity of heat is larger than that which the same elements in their ordinary free state evolve in combining, because, in the form of isolated atoms, they contain an excess of heat, which they give up on passing into their ordinary condition of molecules. The alterations which the elementary bodies experience before entering into true chemical combination, or after separation from that state, are therefore characterised by heat-phenomena which have no connection with those accompanying actual combination and decomposition. Hence the stability of a compound affords no measure of the magnitude of the affinity of its elements. Compounds whose elementary constituents require for their separation equal quantities of heat, will be decomposed with greater facility, the greater the amount of heat which these elements evolve in passing from the nascent state (*i.e.* the state in which they exist in combination and separate from it) into the ordinary state.

A considerable portion of the heat evolved by the chemical action in the battery remains in the calorimeter, and is not available for the performance of useful work in the external part of the circuit. This quantity of heat (= 6,000 units in the experi-

\* In this experiment the distance of the plates was 30 mm., in all the others 5 mm.

ments above described) is that which is due to the passage of the hydrogen from the nascent to the ordinary state.

The quantity of heat which might be supposed to be equivalent to the work expended in the orientation of the molecules of the electrolyte is so small that it may be neglected. The concentration and nature of the liquid, and the distance between the immersed metal plates, likewise exert no appreciable influence on the distribution of heat in the circuit, and therefore, also, do not perceptibly alter its resistance. A greater influence appears to be due to the size of the immersed plates.

The remaining portion of the heat developed by the battery, that is to say the quantity which is transferable to the connecting wire, and capable of doing work outside the battery, may be regarded as the measure of the voltaic energy of the battery.

In another series of experiments (*Compt. rend.* lxxiii. 890, 936) Favre has determined the voltaic energy,  $E$ , of several battery-combinations. That of a Smee's couple was found to be equal to 15,000 heat units. For a Grove's battery, in which the ordinary nitric acid is replaced by fuming nitric acid,  $E = 49,847$  heat-units. A zinc-platinum pair excited by a mixture of permanganic and sulphuric acids, gave  $E = 39,234$  heat-units. The same with hypochlorous acid gave  $E = 50,806$ . A combination, one pole of which was formed of a plate of hydrogenised palladium immersed in dilute sulphuric acid, while the other pole consisted of a platinum plate in solution of cupric sulphate, gave  $E =$  about 4,000 units.

The results obtained in the electrolysis of the principal oxygen-acids are given in the following table, in which column I. indicates the voltaic energy of these acids as directly determined (in the battery); column II. the same as calculated from the number of heat-units transferred from the battery to the acid when the acid is electrolysed in an ordinary non-partitioned voltameter; and column III. the same as determined by electrolysis in a voltameter divided into two cells by a porous diaphragm, so that the separated elements cannot recombine.

	I.	II.	III.
Chromic acid . . . . .	30,225	31,279	34,176
Permanganic acid . . . . .	39,234	42,617	45,304
Fuming Nitric acid . . . . .	49,848	52,822	47,646
Concentrated Nitric acid . . . . .	46,447	46,786	44,190
Hypochlorous acid . . . . .	50,807	55,754	51,908.

For the hydrogen-acids electrolysed in a partitioned voltameter, the following results were obtained:

Hydrochloric acid . . . . .	173,468 heat-units
Hydrobromic acid . . . . .	177,108 "
Hydriodic acid . . . . .	173,629 "

The difference between the first and second of these numbers is equal to that between the second and third.

A Smee's battery in which the sulphuric acid is replaced by one of these three haloid acids, exhibits the following degrees of voltaic energy:

With Hydrochloric acid . . . . .	16,738 heat-units
,, Hydrobromic acid . . . . .	14,967 "
,, Hydriodic acid . . . . .	14,584 "

*Electrolysis of the Oxides and Sulphates of the Alkali-metals.*—These compounds can be decomposed by batteries whose energy is smaller than that which is required to produce the same compounds from their constituents, because the energy of the battery is strengthened by that which is brought into play by the oxidation of the metal. This oxidation is a synelectrolytic effect, *i.e.*, one which takes place in connection with and during the electrolysis. The quantity of heat abstracted from the battery by an alkali subjected to electrolysis is the same for all the alkalis. This quantity of heat (about 50,000 units on the average) is made up of two portions, namely the heat of combination of the water = 34,500 units, and the quantity, equal to rather more than 1,400 units, which is developed by the passage of the liberated constituents of the water from the active into the ordinary state; this last change, which takes place after the electrolysis, is called meta-electrolytic.

The process of decomposition in the salts is exactly similar. If the voltameter containing the salt be divided by a porous diaphragm, so as to prevent the recombination of the acid and base, the quantity of heat evolved is diminished by the heat of combination, and amounts, on the average, to 14,000 units. If the continuous reproduction of the oxide be prevented by pouring mercury into a porous cell, placing the cell in the solution, and surrounding it with a platinum plate forming the positive

pole, so that the metal may be immediately amalgamated at the negative quicksilver surface, the decomposition does not become rapid unless the energy of the battery be considerably increased. A very weak, slow decomposition does indeed take place, because the amalgamated metal undergoes gradual oxidation; from the same cause, also, the strengthened battery attains its full decomposing power at a degree of energy somewhat below that which is indicated by theory (Favre, *Compt. rend.* lxxiii. 767, 1036).

*Electrolysis of various Acids and Salts.*—Experiments on the electrolysis of acetic acid, zinc acetate, formic acid, cupric formate, oxalic acid, sulphuric acid, monohydric phosphate and aqueous phosphoric acid, have led to the following conclusions: When the electrolysis is difficult, as in the case of acetic acid, and the voltaic energy of the battery is small, the secondary reactions, which usually take place after the true electrolysis, and produce heat not transferable to the circuit, always tend to strengthen the energy of the battery. On the other hand, the more the energy of the battery is increased by using a greater number of cells, the less does it appear to be strengthened by the secondary reactions in the voltameter. It is, therefore, very difficult to determine exactly the quantity of heat which is due to the battery and transmissible or not transmissible to the circuit. The secondary actions above spoken of are such as are produced by the hydrogen and oxygen set free during the electrolysis, the first being burned, the second oxidising any combustible substances present (*Compt. rend.* lxxiii. 1186).

In the electrolysis of the sulphates of zinc and copper, and of copper nitrate, in the voltameter, the following quantities of heat were found to be transferred to the voltameter from the battery:

Zinc sulphate . . . .	65,510 heat-units
Cupric sulphate . . . .	39,415 "
Cupric nitrate . . . .	37,770 "

When mixed saline solutions are electrolysed, very different results are obtained, according to the proportions of the mixture, the voltaic energy of the battery, the electric resistance of the salts, and the more or less rapid course of the operation. Sulphuric acid behaves like a salt,  $\text{SO}_4\text{H}^2$ , and its gradual liberation during the electrolysis of zinc or copper sulphate, consequently exerts a continually increasing influence on the amount of heat developed in the decomposition. In fact, a great part of the sulphuric acid set free during the electrolysis of zinc sulphate is electrolysed instead of the zinc salt, because it offers less resistance to decomposition, and consequently less heat is withdrawn from the battery than would be required for the decomposition of the zinc salt. This electrolysis of the sulphuric acid instead of the metallic salt, is greatly augmented when the resistance is increased, as, for instance, by inserting the thermorheostat. The disturbing influence of the sulphuric acid can be avoided by employing a large quantity of zinc solution, about 2 litres, in the voltameter, because when the sulphuric acid formed during the operation is immediately diluted to such an extent, that its electrolysis, in comparison with that of the zinc salt, may be neglected.

When, on the other hand, cupric sulphate is electrolysed, which offers less resistance to its decomposition than sulphuric acid, the quantity of the latter increases rapidly, and it becomes necessary to employ the thermorheostat—(1) in order to render the resistance of the voltameter small compared with the total resistance of the circuit; (2) to retard the electrolysis so far that the cupric sulphate may have time to approach the negative electrode in the same proportion in which it is decomposed, as otherwise the sulphuric acid would be electrolysed in the place of copper-salt.

In electrolysing a mixture of the three sulphates of zinc, cadmium, and copper, Favre has succeeded, by altering the condition of the experiments, in obtaining at will, one metal or two metals at the same time, or all three metals in certain proportions. The results of the operations vary, 1st, with the voltaic energy of the battery; 2d, with the electrolytic resistance of the salts employed; 3rd, with the relative quantity of each salt; 4th, with the more or less rapid progress of the operation, which can be regulated by means of a rheostat.

*Voltameters in which the whole of the hydrogen evolved by decomposition of hydrochloric or hydriodic acid is taken up by free iodine or bromine dissolved in the acid.* According to Favre, the only ones in which the quantity of heat consumed in the decomposition is equal to that which is liberated in recombination. In the electrolysis of cupric sulphate between copper plates this is not the case, although here, also, the heat decomposed is immediately reproduced, but a certain quantity of the voltaic energy transmitted from the battery to the voltameter is converted into heat, and remains in the voltameter as heat not transmissible to the circuit. The conversion of voltaic energy into heat, probably takes place whilst the metal passes from the state

in which it is present in the saline solution into its elementary state, resuming its metallic properties. On the other hand, the copper of the plates, in order to pass from its truly metallic state into that modification in which it exists in its solutions, consumes heat derived from the battery. On making this experiment, first with plates of rolled copper, then with plates covered with electrolytically deposited copper, it is found that the rolled copper possesses less heat than that which is deposited by electrolysis.

If from the 10,500 heat-units evolved during the electrolysis of cupric sulphate between platinum-plates, we subtract 1,000 units due to the separation of copper, we obtain 9,500 units as the thermic expression of the change of state which the oxygen undergoes during its liberation.

The analogous expression for the liberation of 1 equivalent hydrogen is 4,000 heat-units, obtained by subtracting 9,500 from the 13,500 units evolved during the electrolysis of one equivalent of hydrogen sulphate between platinum plates (Favre, *Compt. rend.* lxxiii. 1258).

**ELEMENTS.** The relations between the atomic weights of the elementary bodies and their physical and chemical characters, already explained in the article 'Metals, Atomic Weights, and Classification of' (vol. iii. p. 275, second edition of this Dictionary), have been further developed by Mendelejeff in an elaborate paper (*Ann. Ch. Pharm. Suppl.* viii. 133-229).

Mendelejeff points out that when the elements are arranged according to the order of their atomic weights, from H = 1 to U = 240, the relations between their properties and their atomic weights, exhibit the form of a periodic function. If, for example, the fourteen elements whose atomic weights lie between 7 and 36 be thus arranged:

Li = 7; G = 9.4; B = 11; C = 12; N = 14; O = 16; F = 19.  
Na = 23; Mg = 24; Al = 27.3; Si = 28; P = 31; S = 32; Cl = 35.5.

it is seen at once that the characters of these elements vary gradually and regularly as their atomic weights increase, and that this variation is periodical, i.e. varies in the two series in the same manner, so that the corresponding members of these series are analogous to one another; Na and Li; Mg and G; Al and B; Si and C; S and O, &c. forming similarly constituted compounds, or, in other words, possessing equal atomicity or combining capacity. Moreover the combining capacity of the elements in each series increases regularly with the atomic weight, the first members forming monochlorides, the second dichlorides, the third trichlorides, &c., or corresponding oxides or oxychlorides.

The physical characters of the elements and their corresponding compounds likewise exhibit remarkable regularity when thus arranged, as may be seen with regard to the specific gravities and atomic volumes of the elements in the second series above given:—

	Na	Mg	Al	Si	P	S	Cl
Sp. gr. . .	0.97	1.75	2.67	2.40	1.84	2.06	1.33
At. volume	24	14	10	11	16	16	27
	Na <sup>2</sup> O	Mg <sup>2</sup> O <sup>2</sup>	Al <sup>3</sup> O <sup>3</sup>	Si <sup>2</sup> O <sup>4</sup>	P <sup>2</sup> O <sup>5</sup>	S <sup>2</sup> O <sup>8</sup>	Cl <sup>3</sup> O <sup>7</sup>
Sp. gr. . .	2.8	3.7	4.0	2.6	2.7	1.9	(?)
At. volume	22	22	25	45	55	82	(?)

Most of the other elements may likewise be arranged in groups of seven, the members of which exhibit similar relations, e.g. :—

	Ag	Cd	In	Sn	Sb	Te	I
At. weight .	108	112	113	118	122	125?	127
Sp. gr. . .	10.5	8.6	7.4	7.2	6.7	6.2	4.0

Such a group of seven elements is called by Mendelejeff, a *small period* or *series*.

The elements which can be thus seriated are contained in the first seven columns of the table on p. 463, those in the same column having equal combining capacity, and therefore forming oxides of corresponding composition.

On comparing the several series in this table, it will be observed that the corresponding members of an even, and of the following uneven series (the fourth and fifth for example) differ from one another in character much more than the corresponding members of two even or two uneven series (e.g. the fourth and sixth or the fifth and seventh); thus calcium resembles strontium much more than it resembles zinc. The members of the even series are not so distinctly metalloïdal as those of the uneven series; and the last members of the even series resemble in many respects (in their lower oxides, &c.) the first members of the uneven series. Thus chromium and manganese in their basic oxides are analogous to copper and zinc. On the other hand, strongly marked differences exist between the last members of the uneven series (haloids) and the first members of the following even series (alkali-metals). Now

TABLE I.

Series	Group I. RH RO	Group II. RO	Group III. RO	Group IV. RH RO	Group V. RH RO	Group VI. RH RO	Group VII. RH RO	Group VIII. RO
1. .	H = 1							
2. .	Li = 7	G = 9.4		C = 12	N = 14	O = 16	F = 19	
3. .	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4. .	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59 Ni = 59, Cu = 63
5. .	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6. .	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7. .	(Ag = 108)	Cd = 112	In = 113	Su = 118	Sb = 122	Te = 125	J = 127	
8. .	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	
9. .	(—)	—	—	—	—	—	—	
10. .	—	—	?Er = 175	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199
11. .	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Pi = 205	—	—	
12. .	—	—	—	Th = 231	—	U = 240	—	

between the last members of the even series and the first members of the uneven series there occur, according to the order of the atomic weights, *all* those elements which cannot be included in the small periods. Thus, between Cr and Mn on the one hand, and Cu and Zn on the other, there come the elements Fe, Co, Ni, forming the following transition series:

Cr = 52; Mn = 55; Fe = 56; Co = 59; Ni = 59; Cu = 63; Zn = 65.

In like manner after the sixth series follow the metals Ru, Rh, Pd; and after the tenth, Os, Ir, Pt. These two series of seven terms each, together with the three intervening members, form a *long period* of seventeen members.

As these intermediate members are not included in either of the seven groups of short period, they form a group of themselves (the eighth), some of the numbers of which, viz. Os and Ru, are capable of forming oxides of the form  $RO^2$  or  $R^2O^3$ . This group contains nine metals, viz.:—

Fe = 56;	Ni = 59;	Cu = 59.
Ru = 101;	Rh = 104;	Pd = 106.
Os = 193?	Ir = 195?	Pt = 197.

These metals resemble one another in many respects: (1) They are all of grey colour and difficult of fusion: the fusibility increases from Fe to Co and Ni, just as in the following series Ru, Rh, Pd, and Os, Ir, Pt. (2) They possess in a high degree the power of condensing and giving passage to gases, as seen especially in nickel, palladium, iron, and platinum. (3) Their highest oxides are bases, or acids of little energy, which are easily reduced to lower oxides of more decided basic character. (4) They form stable double cyanides with the alkali-metals. Fe, Ru, and Os, form analogous compounds  $K^2RCy^2$ ; Co, Rh, Ir, form salts having the general formula  $K^2RCy^2$ ; Ni, Pd, Pt, form salts having the composition  $K^2RCy^2$ . (5) All these metals form stable metallammonium salts resembling one another in many of their characters. Thus rhodium and iridium form salts analogous in composition to the rosecobaltic salts  $RX^2 \cdot 5NH^3$ . (6) Some of the compounds of these metals, especially those of the higher degrees of combination, are distinguished by characteristic colours.

The metals Cu, Ag, Au, are also, on account of analogous behaviour, included in the eighth group; although, according to the constitution of their lower oxides, they may also be included in the first group.

The arrangement of the elements in the order of their atomic weights and the composition of the short and long periods, is more clearly seen in Table II., in which the periods form vertical columns:—

TABLE II.

Typical Elements.	K = 39		Rb = 85	Cs = 133	—	—
	Ca = 40		Sr = 87	Ba = 137	—	—
	—		Yt = 88?	Di = 138?	Er = 178?	Th = 231
	Ti = 48?		Zr = 90	Ce = 140?	La = 180?	—
	V = 51		Nb = 94	—	Ta = 182	—
	Cr = 52		Mo = 96	—	W = 184	U = 210
	Mn = 55		—	—	—	—
	Fe = 56		Ru = 104	—	Os = 195?	—
	Co = 59		Rh = 104	—	Ir = 197	—
	Ni = 59		Pd = 106	—	Pt = 198?	—
	Cu = 63		Ag = 108	—	Au = 199?	—
	Zn = 65		Cd = 112	—	Hg = 200	—
H = 1	Li = 7		Na = 23	—	Tl = 204	—
	B = 9.4		Mg = 24	—	Pb = 207	—
	Al = 27.3		—	In = 113	Bi = 208	—
	C = 12		Si = 28	—	—	—
	N = 14		P = 31	As = 75	—	—
	O = 16		S = 32	Se = 78	—	—
	F = 19		Cl = 35.5	Br = 80	—	—
			—	J = 127	—	—

In the members of the even series (Table I.), the metallic or basic character predominates, whereas the corresponding members of the uneven series rather exhibit acid properties. Thus there is a decided difference between V, Nb, Ta, from the even series of the fifth group, and P, As, Sb, Bi, from the uneven series whose highest oxides have a similar constitution  $R^2O^3$ , the former yielding less powerful acids than the latter. The members of the even series do not, so far as is known, yield volatile compounds with hydrogen or the alcohol-radicals, like the corresponding members of the uneven



series; thus all attempts to prepare the compound  $Ti(C^2H^3)^4$  from  $TiCl^4$  have been unsuccessful, in spite of the great resemblance between  $TiCl^4$ ,  $SiCl^4$  and  $SnCl^4$ .

The position of the second series seems at first sight to be inconsistent with the general division of the elements into even and uneven series; for most of the members of this series possess acid properties, form compounds with hydrogen and the alcohol-radicles, and some of them are gaseous—in all which characters they rather resemble the elements of the uneven series. It must, however, be observed, with regard to this series: (1) That it does not include an eighth group like the other uneven series; (2) That the atomic weights of the elements included in it differ from those of the corresponding elements of the following series by only 16, whereas in all the other series this difference ranges from 24 to 28. The difference between the atomic weights of successive even series is generally about 46, but in the elements of the second and fourth series it is only 32–36.

	Li.	G.	B.	C.	N.	O.	F.	Na.	Mg.	Al.	Si.	P.	S.	C.
	K	Ca	—	Ti	V	Cr	Mn	Cu	Zn	—	—	As	Se	Br
Diff.	32	31	—	36	37	36	36	40	41	—	—	44	46	45

These peculiarities explain the apparent anomalies above mentioned, and, moreover, afford additional evidence of the dependence of the properties of the elements on their atomic weights. To make the elements of the second series analogous in character to those of the fourth, their atomic weights should indeed be smaller than they actually are. Similar anomalies may also be observed in comparison of Na with Ca and of Mg with Zn, but they disappear in cases of P and As, S and Se, Cl and Br, where the differences in the atomic weights conform to the general rule.

In consequence of the peculiar properties of the elements of the second series, Mendelejeff designates them as typical elements, to which category, also, belong hydrogen, and likewise sodium and magnesium for the reason just stated. These typical elements may indeed be regarded as analogous to the lowest members of homologous series ( $H^2O$  and  $CH^4O$  for example), which, as is well known, do not exhibit all the properties of the higher homologues.

The preceding considerations likewise explain the isolated position of hydrogen, the element possessing the lowest atomic weight. According to the form of its salifiable oxide  $H^2O$ , and of the salts  $HX$ , it belongs to the first group; its nearest analogue is Na, which likewise belongs to an uneven series of the first group. More remote analogues of hydrogen are Cu, Ag and Au.

Mendelejeff also develops several applications of the law of periodicity: viz. (1) To the classification of the elements. (2) To the determination of the atomic weights of elements whose properties are but little known. (3) To the determination of the properties of hitherto unknown elements, those, namely, which might be expected to occupy the blank spaces in the preceding tables. (4) To the correction of the values of atomic weights. (5) To the completion of our knowledge of the combination-forms of chemical compounds.

For the details of these applications we must refer to the original paper. The proposed corrections of atomic weights will be noticed in connection with the several elements. (See CERIUM, DIDYMIUM, ERBIUM, LANTHANUM, TELLURIUM, YTTRIUM.)

**ELLAGIC ACID.** For Schiff's view of the constitution of this acid, see TANNIC ACID.

**ELVANITE.** Analyses of this rock from Knockmalon, Waterfordshire, and of the clay slate in which it is imbedded, have been made by J. A. Phillips (*Phil. Mag.* [4], xxxix. 12). The elvanite consists of a bluish-grey ground-mass containing crystals of quartz and oligoclase, together with a little hornblende. 1. Elvanite, sp. gr. 2.66. 2. Felsite, sp. gr. = 2.64. 3. Slate, sp. gr. 2.66. 4. Altered state, sp. gr. = 2.65.

$SiO^2$	$AlO^2$	$Fe^2O^2$	$FeO$	$CaO$	$MgO$	$K^2O$	$Na^2O$	$H^2O$	$X^*$
72.33	9.02	6.34	1.06	1.92	trace	1.46	5.83	1.33	0.35
80.50	8.33	3.44	0.96	1.21	trace	1.89	2.12	1.38	0.37
74.28	7.78	7.10	0.90	1.08	0.46	2.05	5.05	0.80	0.34
52.66	18.33	10.43	9.00	1.76	trace	0.73	2.12	5.50	0.50

**EMBRITHITE.** A. Frenzel (*J. pr. Chem.* [2], ii. 360) has analysed the two species of lead sulphantimonite from the Algaitschinski mine, near Nertschinsk, described by Breithaupt under the names plumbostilb (A), and embrithite (B), and finds them both to agree with the formula  $10PbS.3Sb^2S^2$ . (C):—

\* Loss in the water-bath. No. 2 contains a trace of manganese oxide.  
2nd Sup. II H

	Pb	Cu	Sb	S		Sp. gr.
A (found) (1).	59.64	0.88	19.49	18.04	= 98.05	6.12
(2).	59.44	0.88	21.48	18.14	= 99.94	6.12
(3).	not determined	—	21.34 not determined	—	—	6.22
B (found) (1).	59.30	0.80	21.47	18.08	= 99.65	6.32
(2).	59.43	not determined	—	—	—	—
C (calc.)	60.59	—	21.53	17.88	= 100.00	—

In spite of the difference in specific gravity, colour (A is lead-grey to steel-grey, B, pure blue-grey), tenacity (B is softer), and cleavage (A in two directions, B only in one), Frenzel is inclined to regard plumbostib as the cauliform and fibrous, embrittle as the fine-grained aggregation of one and the same species. The hardness of both = 2.5.

**EMETINE.** According to Pander (*Chem. Centralblatt*, 1872, 440), sulphuric acid containing molybdic acid gives, even with only  $\frac{1}{100}$  of a milligram of emetine, a reddish colour quickly changing to green, and with  $\frac{1}{100}$  mgm. a reddish iridescence. Potassium-bismuth iodide and potassium-cadmium iodide give precipitates with  $\frac{1}{10}$  mgm. of this alkaloid in solutions diluted 25,000 times.

**ENAMEL.** The following preparation is recommended in Dingler's *Polytechnic Journal* (cciii, 499) for enamelling the insides of copper vessels used for cooking fruit or vegetables:—12 parts of white fluorspar, 12 parts unburnt gypsum, and 1 part borax are finely powdered, intimately mixed and fused in a crucible. The fused mass is then poured out, and after cooling is rubbed up to a paste. The copper vessel is then coated inside with this preparation, which is applied by means of a brush, and the vessel is left in a moderately warm place, so that the coating may dry uniformly; it is then subjected to a gradually increasing heat, till the preparation melts. On cooling, the vessel is found to be coated internally with a white, opaque enamel, adhering very firmly to the copper, not chipping off by ordinary knocking and rubbing, and impervious to vegetable acids.

**ENNEACHLORDINAPHTHALENE, C<sup>20</sup>H<sup>12</sup>Cl<sup>8</sup>.** This, according to Faust, (*Zeitschr. f. Chem.* [2] vi. 297) is the final product of the action of chlorine gas on heated chloronaphthalenes. After repeated crystallisation from alcohol, it forms soft white needles, melting at 156°–158° (Faust & Saume, *Ann. Ch. Pharm.* clx, 65).

**EOSITE.** A vanadio-molybdate of lead from Leadhills in Scotland. See VANADATES OF LEAD.

**EPIBOULANGERITE.** A sulphantimonite of lead occurring on veins in the Bergmannstrost mine at Altenberg in Silesia, in dark gray needles, of sp. gr. 6.309. Analysis gave, for fine levigated needles, the values A; for coarser material, the values B; and for a boulangerite of sp. gr. 6.825, on which the epiboulangerite rests, the values C:—

	S	Sb	Pb	Ni	Fe	Zn
A.	21.31	20.23	54.88	0.30	0.84	1.32 = 98.88
B.	21.89	20.77	56.11	0.20	0.60	0.20 = 99.86
C.	18.51	20.96	58.73	—	2.13	— = 100.33

Supposing the epiboulangerite to be mixed with a small quantity of zinc blende, analyses A and B lead to the formula 3PbS.Sb<sup>2</sup>S<sup>3</sup> + 3(3PbS.Sb<sup>2</sup>S<sup>3</sup>). (Websky *Jahrbuch für Mineralogie*, 1870, 351).

**EPICHLORHYDRIN.** See CHLORHYDRINS. (P. 320.)

**EPICYANHYDRIN, (C<sup>2</sup>H<sup>3</sup>)<sub>2</sub>CN<sub>2</sub>.**—For the preparation of this compound, discovered by Puzschke (*1st Suppl.* 580), he now recommends the following process: 20 grams of epichlorhydrin are added to a solution of 15 grams of potassium cyanide in 60 grams of water, the violent reaction which immediately takes place being moderated by dipping the vessel into cold water. The epicyanhydrin which separates on cooling from the brown solution may be purified by recrystallisation from alcohol or water. From water it crystallises in broad prisms, often united in rows, which melt at 162°.

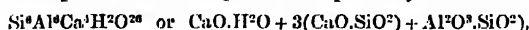
When epicyanhydrin is boiled with potash-ley, a large quantity of ammonia is given off, but the solution turns black, and does not yield the corresponding carbon-acid. Better results are obtained with baryta; but a still more definite reaction takes place on heating the epicyanhydrin for some time to 130° (in a sealed tube) with dilute sulphuric acid. The liquid on cooling deposits shining colourless needles, which, when purified by recrystallisation from hot water, with addition of animal charcoal, and then dried at 100°, exhibit the composition of the acid, C<sup>2</sup>H<sup>2</sup>O.CO<sup>2</sup>H. This acid melts at 225°; its silver salt, C<sup>2</sup>H<sup>2</sup>O.CO<sup>2</sup>Ag, obtained by precipitating the

ammonium salt with silver nitrate, blackens but slightly on exposure to the air, and may be dried without decomposition at 50°-60°.

On mixing the solution of the ammonium salt with lead acetate, the lead salt is precipitated after a while in broad, colourless, transparent laminae.

When epichlorhydrin is added to a solution of potassium sulphocyanate mixed with sulphuric acid, and the liquid is warmed, a fetid oil separates, which solidifies after a while and may be crystallised from alcohol. This compound is probably an addition-product,  $C^3H^2ClO.CNS = C^3H^2ClO + NCSH$  (Pazschko *J. pr. Chem.* [2], i. 82).

**EPIDOTE.** The formula given for this mineral in vol. ii. p. 490, on the authority of Rammelsberg, is  $Si^2Al^2Ca^2O^{36}$  or  $3(2CaO.SiO^2) + 2(2Al^2O^3.3SiO^2)$ , the alumina being more or less replaced by ferric oxide. This formula Rammelsberg has lately sought to confirm by an analysis of the epidote of Sulzbach (*Zeitschr. d. deutsch. geolog. Gesellsch.* 1872. 69). Tschermak, on the other hand, in his memoir on felspars (*Wien. Akad. Ber.* i. 585) first represented the composition of epidote by the formula :



and Kenngott (*Jahrbuch für Mineralogie.* 1871, 449), by a comparison of all the published analysis of epidote, concludes that, with the exception of a few of doubtful character, they may all be concluded in the latter formula, the alumina being more or less replaced by ferric oxide, and the lime to a small extent by magnesia; the presence of the magnesia appears, however, to be due, in many cases at least, to foreign minerals imbedded in the epidote. In some of the analyses, the iron is calculated partly as ferrous oxide; this, however, Kenngott reckons also as ferric oxide, and regards it as taking the place of an equivalent quantity of alumina.

To decide between the two formulae above given, C. Ludwig (*Ann. Ch. Pharm.* clxv. 217) has made a series of analyses of perfectly pure specimens of epidote, free from foreign enclosed minerals, as it occurs in the beautiful transparent crystals from Sulzbach.

This epidote contains silica, alumina, ferric oxide, ferrous oxide, lime, water, and traces of manganous oxide, magnesia, and chlorine. The quantitative analysis was carried out by the processes usually adopted for silicates, excepting that the ferrous oxide was determined by decomposing the mineral with sulphuric acid in a sealed glass tube, and acting upon it with a standard solution of dilute potassium permanganate. Especial care was bestowed on the estimation of the water, as it is chiefly on this point that previous analyses are at variance. Epidote loses about 0.25 per cent. of its weight by ignition in a platinum crucible over a Bunsen's burner, and nearly 2 per cent. when heated in a gas flame fed by a blast of air; after this strong ignition it is reduced to a sintered mass easily attacked by acids. To avoid errors which might arise from reduction of ferric to ferrous oxide by the flame-gases, and obtain a direct demonstration of the presence of water in epidote, the mineral previously dried at 150° was enclosed, in Ludwig's experiments, in a platinum tube through which a slow stream of dry air was passed, and heated to whiteness over a gas-flame urged by a blast, the water evolved being condensed in a calcium chloride tube connected with the platinum tube. The mean of eleven experiments made in this manner, gave from 1.78 to 2.35 per cent. of water, the mean being 2.05.

The mean result of several analyses of the mineral is as follows:—

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	CaO	H <sup>2</sup> O	MnO, MgO, Cl	
or,	37.83	22.63	14.02	0.93	23.27	2.05	traces	= 100.73
	Si	Al	Fe		Ca	H	O	
			as Fe <sup>2</sup> O <sup>3</sup>	as FeO				
	17.65	12.06	9.81	0.72	16.62	0.23	43.64	
The atomic proportions of the elements are therefore—								
	Si	Al	Fe		Ca	H	O	
			as Fe <sup>2</sup> O <sup>3</sup>	as FeO				
	0.630	0.440	0.175	0.013	0.415	0.230	2.727	
		0.615		0.428				
or,	6	5.86		4.07		2.2	25.07	

Tschermak and Kenngott's formula requires—

6	6	4	2	26
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The result of the analysis of perfectly pure epidote is therefore to confirm the formula  $Si^2Al^2Ca^2H^2O^{28}$ .

Epidotes may accordingly be regarded as mixtures of two isomorphous constituents  $\text{Si}^2\text{Al}^2\text{Ca}^1\text{H}^2\text{O}^{22}$  (aluminium epidote) and  $\text{Si}^2\text{Fe}^2\text{Ca}^1\text{H}^2\text{O}^{22}$  (iron epidote).

The percentage composition of these two varieties in the pure state is as follows:—

	Aluminium Epidote	Iron Epidote
Silica . . . . .	39.543	33.272
Alumina . . . . .	33.875	—
Ferrie oxide . . . . .	—	44.362
Lime . . . . .	24.605	20.702
Water . . . . .	1.977	1.664

Ludwig's paper contains a table of the percentage composition of such mixtures calculated for 1, 2, 3 . . . . . up to 45 p.c. of iron epidote, and a comparison of these calculated numbers with all the actual analyses of epidote hitherto published,—excluding, however, as inaccurate, those which take no account of the water, and in which nevertheless the sum of the other constituents is equal to or greater than 100, also those which indicate a considerable amount of magnesia or alkalis, these having been made upon impure material.

The result of this comparison is to show that the older analyses of epidote also lead to the formula  $\text{Si}^2\text{Al}^2\text{Ca}^1\text{H}^2\text{O}^{22}$ .

Epidote from the Untersulzbach valley in Salzburg (sp. gr. 3.51), has been analysed by F. Kottal, in Lieben's laboratory, with the following mean results:—

$\text{SiO}^2$	$\text{Al}^2\text{O}^3$	$\text{Fe}^2\text{O}^3$	$\text{Fe}^2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{H}^2\text{O}$
37.00	22.10	13.80	0.33	25.15	0.03	0.26 = 98.67

These numbers do not differ much from those obtained by Ludwig, excepting in the water, which was determined by igniting the substance, previously dried at  $100^\circ$ , in a stream of carbon dioxide. Probably the degree of heat applied was not sufficient to expel the whole of the water (*Ann. Ch. Pharm.* clxv. 360).

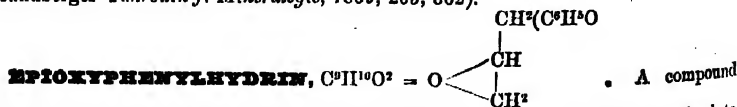
The most highly ferruginous epidotes are those from Switzerland and the Fornazza valley; in these the ratio of alumina to ferrie oxide is  $5\text{Al}^2\text{O}^3 : 1\text{Fe}^2\text{O}^3$ ; in the epidotes from Bourg d'Oisans in Dauphiny, Traversella in Piedmont, Arendal in Norway, and Penig in Saxony, the ratio is  $2\text{Al}^2\text{O}^3 : 1\text{Fe}^2\text{O}^3$ .

**EPIGENITE.** A cuproso-ferrous sulphide from the Neuglück mine near Wittichen in Baden, where it is found in short prismatic rhombic crystals exhibiting the combination  $\infty\text{P} . m\bar{\text{P}}\infty . m\text{P}\infty$ , and having the angle  $\infty\text{P} : \infty\bar{\text{P}} = 110^\circ 50'$  nearly. Colour steel-grey with black streak and black and blue tarnish. Hardness = 3.5. When heated in a tube, it yields a sublimate, first of sulphur, then of sulphide of arsenic, a reaction which is likewise exhibited by enargite, and indicates the presence of arsenic pentasulphide. It dissolves in nitric acid without separation of sulphur.

Analysis A is by Petersen (*Pogg. Ann.* cxxxvi. 502). As perfectly pure crystals are free from bismuth, and, on the other hand, wittichenite (copper-bismuth sulphide) is imbedded in the baryta of the gangue, the bismuth, together with corresponding quantities of copper and sulphur, has been deducted, giving the corrected result B, which leads to the formula  $6\text{RS}.\text{As}^2\text{S}^3$ , in which  $6\text{RS} = 3\text{Cu}^2\text{S} + 3\text{FeS}$ . The calculated numbers according to this formula are given under C. Silver and zinc were found only in traces.

	S	As	Bi	Fe	Cu
A (found) . . .	31.57	12.09	2.12	13.43	40.32 = 99.53
B (corr.) . . .	32.34	12.78	—	14.20	40.68 = 100.00
C (calc.) . . .	33.58	14.32	—	16.03	36.07 = 100.00

(Sandborger *Jahrbuch f. Mineralogie*, 1869, 205, 862).



formed by heating epichlorhydrin with a solution of potassium phenate in absolute alcohol. On addition of water it separates as an oil which solidifies after being heated to  $200^\circ$ , and may be purified by pressure and recrystallisation from alcohol. The crystals are rhombic, exhibiting the combination  $0\text{P} . \infty\text{P}$ , and having the axes  $a : b$  in the ratio of 0.64076 : 1 and the angle  $\infty\text{P} : \infty\bar{\text{P}} = 65^\circ 20'$  (Lippmann, *Wien. Akad. Ber.* lxii. [2], 605).

**EPISTILBITE.** The crystals of this mineral from the almond-stone of the Finkenhübel near Glatz in Silesia—where it occurs with other zeolites, viz. laumontite, heulandite, desmin, harmotome, and chabasite—have been measured by Websky (*Zeitschr. d. deutsch. geolog. Gesellsch.* xxi. 100), whose angular measurements agree

essentially with those of G. Rose. He regards epistilbite as a mineral species distinct from heulandite.

**ERBIUM.** The compounds of this metal have lately been examined by Clève and Hoeglund (*Bull. Soc. Chim.* [2], xix. 193). They will be described in connection with the yttrium compounds.

**ERGOT.** The constituents of ergot have been examined by J. C. Herrmann (*N. Rep. Pharm.* xx. 283) and by J. B. Gausser, *ibid.* 301). Herrmann, by thoroughly exhausting finely powdered ergot with ether, ultimately obtained six ounces of a fatty oil which, when saponified with soda-ley, yielded a distillate containing ammonia, trimethylamine, and a liquid from which common salt separated a soap, the aqueous portion containing glycerin. This soap, treated with sulphuric acid, yielded a semi-solid oil, and the aqueous liquid from this operation yielded, on distillation, traces of butyric and acetic acid. By pressing this semi-fluid oil between bibulous paper, a solid fat was obtained which, after several recrystallisations from alcohol, melted constantly at  $62^{\circ}$ , solidified at  $57^{\circ}$ – $58^{\circ}$ , and exhibited the composition of palmitic acid. The oil was not a drying oil, and the fluid portion treated with nitric acid yielded claidic acid, whence the presence of oleic acid was inferred.

By treating a portion of the extracted oil with alcoholic ammonia, separating the alcoholic liquor from the oily portion and evaporating, a dark-brown aromatic-smelling residue was obtained, agreeing in properties (excepting its solubility in ether) with the ergotine of Wiggers (ii. 499.)

Contrary to the statements of Manassewitz, the oil was found to be saponifiable with caustic potash, the soap being softer than that obtained with soda.

By exhausting ergot with water, precipitating with lead acetate, and treating the filtrate with mercuric chloride, a precipitate was obtained from which the cecolino of Wenzell was separated, either by treatment with lead oxide or basic lead carbonate or by Wenzell's process, viz., treatment with hydrogen sulphide, and then successively with freshly precipitated silver phosphate, milk of lime, and ammonia carbonate. The product, freed by heat from excess of ammonia carbonate, had an alkaline reaction, and gave white precipitates with mercuric chloride, tannic acid, and potassium cyanide; yellow with phosphomolybdic acid; orange with platonic chloride; red-brown with iodised potassium iodide; and brownish with gold chloride.

The ashes of ergot were found to have the following composition:—

NaCl	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>
1.51	30.06	0.65	1.38	4.88	0.59	0.86	0.26	45.12	14.67 = 99.98

According to Gausser, finely powdered ergot yields, by extraction with ether, 30 p.c. of its weight of fatty oil, containing a resin separable from the fats by nearly absolute alcohol, and giving to them a peculiar bitter rough taste and brownish tint. With lead oxide these fats form a plaster from which ether extracts lead oleate; with soda-ley of 1.3 sp. gr. a soap is obtained; no free ammonia distils over during the operation, the distillate being neutral; on the addition of hydrochloric acid, however, thick white clouds are formed, and the colourless distillate becomes reddish.

The oil readily yields claidic acid with nitric acid. A dose of 10 grams, given in two portions of 6 and 4 grams each, only produced a sensation of nausea, without actual vomiting; the last 4 grams increased the pulse and produced a slight faintness and perspiration, all symptoms ceasing in five hours. The oil extracted with alcohol yielded a resin and a small quantity of crystals, giving the cholesterol reactions; this resin possesses the same physiological properties as the oil, but in a much more marked degree.

Pulverised ergot heated, *per se*, in a water-bath in a retort, gave no volatile bases; and the same was found on heating 250 grams of ergot with 150 of calcium carbonate and 500 of water; but the residue from the ether-extract of the fatty acids had a strong smell of horring-pickle (trimethylamine), and, on distillation with oxalic ether, yielded a distillate containing ammonia and emitting the smell of animal oils; the residue in the retort from this operation, distilled with water, gave ammonia and a smell of animal oils. Hence neither ammonia nor trimethylamine pre-exists in ergot, but these bodies are formed by decomposition of other substances by the re-agents employed.

By boiling with water the residue left after extraction of ergot with ether, precipitation with lead acetate, and of the filtrate with mercuric chloride, a precipitate is obtained which, when treated successively with freshly precipitated silver phosphate, milk of lime, and carbonic acid, yields finally, after evaporation, a brown, hygroscopic, amorphous powder of cecolino; this is soluble in water and alcohol, insoluble in ether and chloroform; on boiling it with potash, ammonia is evolved; it has a bitter taste with sweet after-taste, and, in small doses, produces nausea and

vomiting. The filtrate from the mercury precipitate of ecboiline, on precipitation with phosphomolybdic acid, and digestion of the precipitate with barium carbonate, and evaporation, furnishes ergotine as a greenish-yellow, glistening, amorphous, hygroscopic powder. This base forms deliquescent salts, the hydrochloride crystallising in long slender needles; given to a young dog in small doses, it produced symptoms of nausea without actual vomiting.

On distilling with sulphuric acid the aqueous extract from the ergot deprived of fats by ether, an acid of peculiar odour was obtained which reduced silver nitrate (ergotic acid); on distilling it with alcohol and sulphuric acid, formic ether was found in the distillate.

On extracting the residue deprived of fats by ether, with alcohol of 80 p.c., a cherry-red tincture is obtained, which deposits flocks of a sugar which reduces a potassium-cupric solution (identical with mycose?).

3.2 p.c. of albumin was found in the infusion of ergot, also potash, lime, and magnesia, together with hydrochloric, sulphuric, and phosphoric acids (Ganser).

**ERICACEÆ.** *Gaultheria procumbens* and *Epigaea repens* contain arbutin, ursone, ericolin, tannic acid, a principle analogous to gallic acid, formic acid (in *Epigaea*), glucose, gum and colouring matter. Arbutin, ursone and ericolin have previously been found in *Uva ursi* and *Chimaphila umbellata*, and may, therefore, be regarded as common to plants of the ericaceous order (J. Oxley, *Pharm. J. Trans.* [3], ii. 1050).

**ERSBYITE.** This mineral occurs at Pargas in Finland, intergrown with blackish-green augite (in small quantity) and brown titanite, in some parts, also, with laminar calcspar. It is colourless when quite fresh, and does not exhibit any crystalline faces. Its specific gravity is 1.723.

Considerable uncertainty has hitherto existed respecting the constitution of this mineral. A. E. Nordenskjöld described it as a triclinic feldspar, cleavable in two directions inclined to one another at an angle of  $90^{\circ} 22'$ , and, according to an analysis made by N. A. Nordenskjöld ( $54.13 \text{ SiO}_2$ ,  $29.23 \text{ Al}_2\text{O}_3$ ,  $15.16 \text{ CaO}$ ,  $1.07 \text{ water}$ ), as a true labradorite free from soda. But according to the theory of Tschermak, which regards the triclinic feldspars as isomorphous mixtures of albite and anorthite there should be no such thing as an oligoclase free from lime or a labradorite free from soda. (See FELSPAR.)

To clear up this doubt, G. vom Rath has subjected the mineral to a fresh examination. He finds that it cleaves very distinctly and with equal precision in two directions at right angles to each other, has a specific gravity of 1.723, loses by ignition 0.58 p.c. and gives by analysis—

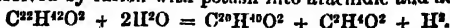
$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	
44.26	30.37	20.17	0.15	1.15	2.75	= 98.85

If the loss in the analysis be attributed to lime and the alkalis, these numbers agree very nearly with the formula of scapolite,  $3\left(\frac{2}{3}\text{CaO} + \frac{1}{3}\text{Na}_2\text{O}\right) \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$  (calc. 44.39  $\text{SiO}_2$ , 30.4  $\text{Al}_2\text{O}_3$ , 21.75  $\text{CaO}$ , and 3.44  $\text{Na}_2\text{O}$ ).

Both the cleavage and the chemical composition of ersbyite show, therefore, that it belongs, not to the calcio-sodic feldspars, but to the scapolites (*Pogg. Ann.* cxliv. 375).

**ERUCIC ACID,**  $\text{C}^{22}\text{H}^{42}\text{O}_2$ . This acid has been obtained by Fitz (*Dent. Chem. Ges. Ber.* iv. 442), from the fat oil of grape-seeds, which exists in them to the amount of 15 to 18 p.c. This oil was saponified with potash, and the acids were separated by the partial precipitation of their alcoholic solution with lead acetate, the first fractions being flocculent, the latter semifluid. The flocculent precipitate, on being treated with warm ether, left a small portion undissolved, the acid from which, by its melting point and analysis, proved to be a mixture of palmitic and stearic acids. The acid contained in the soluble lead salt crystallised from alcohol in lustrous needles, and on analysis was found to be erucic acid. The solubility of its lead salt varies extremely with the temperature, as it is very soluble in ether, benzene, or acetone when hot, and but slightly when cold. One half of the mixed acid contained in the oil was found to be erucic acid, and the remainder an acid yielding a semi-fluid lead-salt, together with a very small quantity of palmitic and stearic acids. By treatment with nitrous acid, the erucic acid was converted into the corresponding clausic acid (brassicic acid), which melts at  $56^{\circ}$  (at  $60^{\circ}$  according to Haussknecht, *1st Suppl.* 367). The lead salt is almost insoluble in warm ether.

Erucic acid is resolved by fusion with potash into arachidic and acetic acids:



This is the usual mode of decomposition of the acids of the acrylic series.

**ERYTHRITE,**  $\text{C}_4\text{H}^{10}\text{O}_4 = (\text{C}_2\text{H}_5)_2(\text{OH})_2$ . Some of the haloïd ethers of this alcohol have been prepared and examined by P. Champion (*Compt. rend.* lxxiii. 114).

**Erythritic Dibromhydrin**,  $C^4H^8Br^2O^2 = (C^4H^7)^2Br^2(OH)^2$ .—When erythrito is treated with a saturated solution of hydrobromic acid in a sealed tube at the temperature of  $110^\circ$  for three hours, a brown liquid is obtained, which, when evaporated on the water-bath and redissolved in boiling ether, deposits crystals of erythritic dibromhydrin. This body is insoluble in water, slightly volatile at  $100^\circ$ , melts at  $130^\circ$ , and forms a crystalline mass on cooling. In its composition and properties it resembles the erythritic dichlorhydrin prepared by De Luyne (1st Suppl. 583).

**Erythritic Dinitrodibromhydrin**,  $C^4H^8Br^2(NO^2)^2O^2$ .—When erythritic dibromhydrin in powder is introduced into a cold mixture of 1 part fuming nitric acid, and 2 parts concentrated sulphuric acid, the temperature slowly rises, and if, after a contact of some minutes, the whole be poured into cold water, a white flaky precipitate is formed, which, after being washed and dissolved in boiling alcohol, deposits the dinitrobromhydrin in long white flexible needles. This body is insoluble in water; melts at  $75^\circ$ ; does not detonate when struck, like nitroerythrite; is decomposed by heat, producing yellow fumes. A boiling solution of potash changes it, the liquid becoming brown, and a nitrate being formed.

**Erythritic Dinitrodichlorhydrin**,  $C^4H^8Cl^2(NO^2)^2O^2$ .—This body, like the preceding, is obtained by the action of a mixture of nitric and sulphuric acids on erythritic dichlorhydrin. It crystallises easily from alcohol, melts at  $60^\circ$ , and resembles the preceding compound in its properties.

**ERYTHROCENTAURIN**. Méhu has demonstrated the identity of the erythrocentaurin prepared from *Erythraea Centaurium* (1st Suppl. 584), with the preparation obtained from *Erythraea chilensis*. The two preparations agree in their solubilities in various liquids, their melting point ( $136^\circ$ ) and in the change of colour from white to red produced by the action of the sun's rays (*J. Pharm.* [4], xi. 454).

**ESENBECKIA**. The bark of *Esenbeckia febrifuga* (Martius) contains, together with much chlorophyll, sugar, gum, and pectous substances (no starch), two very closely allied resinous substances, namely, an acid called esenbeckic acid, resembling quinic acid, and a nitrogenous base, esenbeckine, which crystallises in octohedrons (*C. am Ende, Arch. Pharm.* [2], cxliii. 112).

**ESERINE**. To prepare the neutral sulphate of this base, the hydro-alcoholic extract of the Calabar bean (*Physostigma venenosum*) is dissolved in a small quantity of distilled water, and filtered. To the filtrate is added 1 gram of potassium bicarbonate for every 20 grams of extract dissolved, and the solution is agitated with a considerable quantity of ether. After allowing the ether to separate, it is decanted, and the aqueous liquid again treated with ether, until the whole of the alkaloid is completely removed. The ethereal solution, after the addition of a little distilled water, is carefully neutralised with dilute sulphuric acid containing 40 grams of the monohydrated acid per litre, the point of saturation being ascertained by the aid of good litmus paper. The ether is then gently evaporated or decanted, and the solution of eserine sulphate concentrated to crystallisation. The first crop of crystals is sufficiently pure for medicinal use, but it is preferable to treat the alkaloid again with alkali and ether, which, after a second crystallisation, will render the salt perfectly white and pure.

In preparing a solution of the alkaloid, if as many grams of liquid are obtained as it was found necessary to employ drops of the standard sulphuric acid, 1.0 gram of the solution will contain 0.01 gram of eserine. For general purposes, one part of the above solution may be diluted with 4 or 5 parts of distilled water (*A. Petit, J. Pharm.* [4], xiv. 255).

**Blue Colouring Matter from Eserine**.—Eserine, exactly neutralised with dilute sulphuric acid, then treated with excess of ammonia and evaporated to dryness in a water-bath, yields a residue of magnificent blue colour, soluble in water and alcohol, and crystallising in the form of elongated prisms. This residue stains the skin, nails, &c., and strongly dyes silk blue without the aid of a mordant; acids change the colour to a fine violet purple.

Eserine treated with ammonia, without previous saturation with sulphuric acid, yields, on evaporation, a greenish residue, much less soluble, and turned red by acids (*A. Petit, Compt. rend.*, lxxii. 669).

**ESSENTIAL OILS**. See OILS, VOLATILE.

**ETHANE**,  $C^2H^6$ . On the nitro-derivatives of this hydrocarbon, see NITRO-COMPOUNDS.

**ETHENE**,  $C^2H^4$ . See ETHYLENE.

**ETHYL ALCOHOL,  $C^2H^5O$ .** *Formation from Acetic Acid* (Saytzeff, *J. pr. Chem.* [2] iii. 76. Acetic acid cannot be directly converted into ethyl alcohol by the action of reducing agents, but by first converting it into acetyl chloride by distillation with phosphorus pentachloride, and subjecting this chloride to the action of nascent hydrogen, ethyl alcohol is produced. The reduction is effected by the action of sodium amalgam on a mixture of acetyl chloride and glacial acetic acid, the sodium amalgam decomposing the acetic acid and evolving hydrogen, which then acts on the acetyl chloride, apparently changing it first into aldehyde:  $C^2H^3OCl + H^2 = HCl + C^2H^4O$ , which, by the further action of hydrogen, is converted into alcohol; a fresh quantity of acetyl chloride then converts this alcohol into acetic ether, which is the final product of the reaction. Simultaneously with this process another reaction occurs, whereby, at the expense of the acetyl chloride and the sodium acetate, acetic anhydride is formed, and this by the nascent hydrogen is also converted into alcohol, which, as in the first case, is obtained as acetic ether. This is shown by treating a mixture of either propionyl chloride or butyryl chloride and acetic hydrate with sodium amalgam, when, besides the particular alcohol, ethyl alcohol is also obtained, which can only be formed from the mixed anhydrides generated by the reaction, since acetic acid cannot be directly changed into ethyl alcohol by deoxidising agents. The details of the process are as follows:

Solid sodium amalgam, finely divided, and consisting of 100 parts mercury and 3 parts sodium, was placed in a flask fitted to the lower end of a condenser, and immersed in ice-water. To  $1\frac{1}{2}$  molecules of the sodium a mixture of 1 molecule of acetyl chloride and 2 molecules of acetic hydrate was taken, and gradually poured upon the amalgam, keeping the flask constantly agitated, or stirring its contents briskly with a glass rod passing through the cork. After running in all the mixture, the flask was still kept in motion until its contents had become a solid mass, and the whole was then set aside till the next day. Water was then added, and the mixture distilled until oily drops ceased to come over with the water. The distillate consisted of two layers, the upper of which had a strong odour of acetic ether, and when distilled with potash yielded ethyl alcohol. In this way, 8 grams of alcohol were obtained from 60 grams of acetyl chloride.

On the formation of Ethyl Alcohol from Acetic Anhydride, see 1st Suppl. 592.

*Preparation from Lichens.*—The large quantity of amylaceous matter contained in certain lichens, renders them available for the preparation of spirit, the starch being first converted into glucose by the action of hydrochloric or sulphuric acid, and the glucose fermented in the ordinary way. S. Stenborg (*J. pr. Chem.* civ. 441) prepares alcohol in this manner from reindeer moss (*Cladonia rangiferina*). The lichen, if impure, is treated with 7 p.c., if pure and dry, with 10 p.c. of hydrochloric acid of sp. gr. 1.165, to convert it into sugar; the acid is neutralised with chalk, or better with sodium carbonate (so that the refuse of the operation may be used as fodder for cattle); and the mash is diluted till it contains only 5 p.c. of sugar, which is found to be a good strength for fermentation. By this latter process,  $\frac{1}{10}$  to  $\frac{1}{15}$  of the glucose present, which amounts to 60.68 p.c. of the dry lichen, is converted into alcohol. The spirit obtained by distilling the fermented liquor, has a faint taste of almonds, unless the lichen used is contaminated with pine cones and needles, in which case it has a flavour of gin. The fusel oil, which is quite different from that of corn or potatoes, may be easily removed with charcoal, and the spirit obtained yields by oxidation very good acetic acid. Observations on this process have been published by Stahlschmidt (*Dingl. polyt. J.* cxvii. 177; *Jahresb. f. Chem.* 1870, 1212).

*Defuselation of Spirit.*—W. Artus (*Dingl. polyt. J.* xcvi. 175) removes the fusel oil from spirit, without distillation, by repeated treatment with lumps of charcoal of the size of peas, previously impregnated with pure alumina (by soaking them in solution of alum and sodium carbonate) and then ignited.

On the composition of the 'first runnings' of crude spirit, see ALDEHYDES (p. 82).

*Preparation of Absolute Alcohol.*—Mendelejeff (*Zeitschr. f. Chem.* 1865, 260), who has found quick lime superior to all the other substances in use for dehydrating alcohol, states that, to obtain the alcohol absolute, spirit of sp. gr. not above 0.792 must be taken, and its digestion over the quick lime continued for not less than two days, or else for a few hours at 50°–60°. Even then, on distilling, only the middle portions are found to be anhydrous.

Erlenmeyer (*Ann. Ch. Pharm.* clix. 249) finds that when the spirit is boiled with the lime in a vessel fitted with inverted condenser, for  $\frac{1}{2}$ –1 hour and then distilled, the whole product obtained is anhydrous. If the spirit contains more than 5 per cent. of water, it is only necessary to repeat the treatment with lime two or more times. But with weak spirit, care must be taken at first not to fill more than half the space occupied by the spirit with lime, as otherwise the vessel may be broken by the sinking of



the time. In this way several litres of spirit may be converted in a few hours into absolute alcohol.

**Reactions.**—1. *With Sulphuric Acid.*—Erlenmeyer (*Ann. Ch. Pharm.* clxii. 373) has examined the action of sulphuric acid on alcohol and ether, with results agreeing in the main with those of former experimenters (ii. 437), though differing in certain particulars.

(a). *Formation of Ether from Alcohol, and vice versa, in presence of dilute Sulphuric acid, at high temperatures.* Ether, heated in a sealed tube to 180° with 4 volumes of water and 1 c.c. dilute sulphuric acid, gave a considerable quantity of alcohol. Alcohol heated in sealed tubes with water only, gave no ether. Alcohol heated with dilute sulphuric acid (1 : 3, 1 : 5, and 1 : 10) to 226°–230° yielded ether, ethylene, and, under certain conditions, ethylsulphuric acid.

Hence Erlenmeyer concludes that—

- (1). Alcohol or ether heated with sulphuric acid and water at a high temperature, forms ethylsulphuric acid.
- (2). At a certain temperature, and with a given proportion of alcohol in the solution, ethylsulphuric acid is decomposed into sulphuric acid and alcohol.
- (3). At a higher temperature, or by having a larger proportion of alcohol in the solution, ethylsulphuric acid and alcohol react so as to form ether.
- (4). A part of the ethylsulphuric acid is decomposed, forming ethylene and sulphuric acid, another part forming ethylene, sulphur dioxide and water.

(b). *Formation of Ether from Alcohol under the influence of Neutral Ethylic Sulphate and Ethylsulphuric acid.* Ethylic sulphate heated with the proper proportion of alcohol yields ether when distilled, and ethylsulphuric acid together with free sulphuric acid in the residue; this residue heated to 140°, alcohol being allowed to flow on it, yields ether. Erlenmeyer therefore thought that the formation of ethylic sulphate might probably precede that of ether. But by experiment it was found that alcohol distilled with sulphuric acid, at a temperature at which ethylic sulphate could not form (96°), gave a large percentage of ether in the distillate, no ethylene or sulphurous acid being produced. The formation of ether at this temperature was, however, much slower than at 140°.

2. *With Salts* (Krant, *Ann. Ch. Pharm.* clvi. 323). Zinc acetate acts on alcohol, in the absence of water, at ordinary temperatures, but very slowly; on leaving together for  $7\frac{1}{2}$  months a mixture of 1 mol. zinc acetate with 25 mols. alcohol, about 8 per cent. of the zinc acetate was decomposed. A mixture of 1 mol. of the acetate with 10 mols. alcohol, heated for 10 hours to 100°, showed a separation of 64.75 per cent. of the ZnO employed. From a similar mixture heated for 10 hours to 200°–220°, 97.1 per cent. ZnO had separated.

1 mol. zinc acetate heated with 10 equivs. alcohol to 100°, gave in

6	10	15	30	50 hours.
52.2	61.75	77.4	90.2	93.5 per cent. ZnO.

1 mol. zinc valerate heated with 10 equivs. alcohol to 100°, gave in

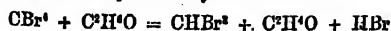
10	20	30	50 hours.
36.4	61.1	71.2	78.9
37.8	62.4	71.8	79.6

The formation of ethyl formate was observed in the action of alcohol on zinc formate, but the difficulty of drying the zinc salt completely, without some decomposition, rendered it unsuitable for comparative experiments.

Alcohol was found to act on the acetates of ammonium, magnesium, mercurous, and silver, with formation of ethyl acetate. At 100°, it had no action on sodium acetate.

3. *With the Chlorides of Sulphur.*—Absolute alcohol treated with either of the chlorides  $S^2Cl^2$  or  $SCl^2$ , is converted into ethylsulphuric acid. The product, diluted with water, and saturated with barium hydrate, yields barium ethylsulphate  $(C^2H^5)_2Ba/S^2O^8 + 2H^2O$  (W. Housser, *Ann. Ch. Pharm.* cli. 249).

4. *With Carbon Tetrabromide.*—Alcohol heated with carbon tetrabromide to 100° for twelve hours, yields bromoform amounting to about three-fourths of the carbon tetrabromide, together with aldehyde and hydrobromic acid.



(Boles & Groves, *Chem. Soc. J.* [2], ix. 784).

*Detection of Alcohol.*—The presence of alcohol when mixed with a large quantity of water may be detected by means of benzoyl chloride, which is very slowly decomposed

by water either cold or lukewarm, but is immediately converted into ethyl benzoate by any alcohol that may be present. The ethyl benzoate remains mixed with the excess of benzoyl chloride, but may be detected by heating a drop of the chloride with aqueous potash, which dissolves the chloride almost immediately, without at first acting on the ethyl benzoate, which may then be recognised by its odour. The reaction is very distinct in working with 20 to 25 c.c. of water containing a hundredth part of alcohol. Even with a thousandth part, the smell of the benzoic ether is very apparent when several cubic centimeters of liquid are used (Berthelot, *Compt. rend.*, lxxiii. 496).

For the detection of alcohol by Lieben's method of converting it into iodoform (1st Suppl. 593), the following mode of proceeding is recommended by H. Hager, (*Zeitschr. anal. Chem.* ix. 492). The reagents used are a solution of potassium iodide in five or six times its weight of water supersaturated with iodine, and a solution of potassium hydrate of the strength of 10 per cent. The clear liquid is heated to 40°-50° with five or six drops of the potash-solution, and the iodine-solution is then added, with gentle agitation, till the liquid becomes somewhat yellowish-brown. If this colour does not disappear on agitation, a drop or more of the potash-solution is added with a glass rod till complete decoloration takes place. The resulting iodoform is then deposited at the bottom of the test-tube in yellow crystals.

If the body to be tested is not soluble in water, it must be shaken up with 5 to 10 times its volume of lukewarm water, the liquid filtered, and the filtrate tested as above.

To detect alcohol in chloroform, the latter is briskly shaken with about 5 times its volume of water, then warmed to 30° or 40°, again shaken till the liquid appears milky from finely divided chloroform, and the chloroform is separated from the watery liquid by filtration through a wet filter.

A. Blachez (*J. Pharm.* [4], ix. 289) detects alcohol in chloroform by introducing a few grams of the liquid into a test-tube, adding a stick of potash as dry as possible, agitating for five minutes, then removing the potash, shaking the chloroform with an equal volume of water, and adding a small quantity of solution of cupric sulphate. If alcohol is present, a precipitate of cupric hydrate is formed by the potash, which the alcohol dissolves. Pure chloroform does not give this reaction, inasmuch as potash is not dissolved by it. A. Vogel (*Zeitschr. anal. Chem.* viii. 473) adds pyrogallie acid to the potash-solution decanted from the chloroform; if a yellowish or brownish colour is then produced on exposure to the air, the presence of alcohol may be inferred. A simpler, though perhaps less delicate method, is to place a few drops of the chloroform, after agitation with potash, on red litmus-paper, the presence of alcohol being then indicated by the production of a blue spot.

**Mixtures of Alcohol and Water.**—The specific heats, heat of combination, boiling point, capillarity, expansion by heat, and compressibility, of mixtures of water and absolute alcohol in various proportions, have been determined by Dupré a. Page (*Phil. Trans.* 1869, 591-614; *Proc. Roy. Soc.* xvii. 333; *Phil. Mag.* [4], xxxviii. 158; *Pogg. Ergänzungsband*, v. 221; *Jahresb.* 1869, 95).

The results are given in the following tables, in which the 'calculated values' of the several physical properties are determined on the supposition that the effect of each constituent of the mixture on the property in question is proportional to its weight.

The greatest differences between the observed and calculated values take place in mixtures containing between 30 and 45 p.c. of alcohol; 30 p.c. corresponds nearly with the formula  $C^2H^6O + 6H^2O$  (= 29.87 p.c.); 45 p.c. nearly with  $C^2H^6O + 3H^2O$  (= 46 p.c.). The excess of the specific heat of any mixture above its calculated amount is approximately equal to the quotient obtained by dividing the number of heat-units evolved in the formation of the same mixture by 3.411, and the depression of the boiling point is approximately equal to the quotient obtained by dividing the coefficient of capillary elevation by 3.6.

#### Heat of Mixture of Alcohol and Water.

Weight per cent. of Absolute Alcohol	Heat-units for 5 grams of Mixture
90 . . . . .	7.7025
80 . . . . .	12.4775
70 . . . . .	18.8200
60 . . . . .	27.2620
50 . . . . .	35.5850
45 . . . . .	38.8095
40 . . . . .	44.8630
30 . . . . .	47.0800
20 . . . . .	43.9545
10 . . . . .	28.6850

*Specific Heat of Mixtures of Alcohol and Water.*

Weight per cent. of Absolute Alcohol	Specific Heat referred to Water = 100		Difference
	found	calculated	
5	101.502		
10	103.576	96.043	+ 7.533
20	104.362	92.086	12.276
30	102.602	88.129	14.473
40	96.805	84.172	12.633
45	94.192	82.193	11.999
50	90.633	80.215	10.418
60	84.332	76.258	8.074
70	78.445	72.301	6.144
80	71.690	68.344	3.346
90	65.764	64.387	1.377
100	60.430		

*Boiling Points of Mixtures of Alcohol and Water.*

Weight per cent. of Absolute Alcohol	Boiling Point		Difference
	observed	calculated	
0	99.4°		
10	90.98	97.25°	— 6.27
20	86.50	95.10	8.60
30	84.01	92.95	8.94
40	82.52	90.90	8.38
45	81.99	89.72	7.73
50	81.33	88.60	7.27
60	80.47	86.50	6.03
70	79.61	84.35	4.74
80	78.84	82.20	3.36
90	78.01	80.05	2.04
100	77.89		

*Capillary Heights of Mixtures of Alcohol and Water in a tube of 0.584 mm. diameter, at 16°.*

Weight per cent. of Alcohol	Height		Relative Molecular Attraction	Height calculated	Difference
	observed	referred to Water = 100			
0	49.47	100	100	100	
10	34.22	69.17	68.07	93.11	— 25.04
20	27.92	56.43	54.83	86.22	31.39
30	23.84	48.19	46.15	79.34	33.19
40	22.41	45.30	42.56	72.45	29.89
45	21.64	43.74	40.64	69.00	28.36
50	21.24	42.93	39.43	65.56	26.13
60	20.93	42.30	37.89	58.68	20.79
70	20.66	41.76	36.42	51.79	15.37
80	20.43	41.29	35.03	44.90	9.87
90	20.06	40.54	33.35	38.02	4.67
100	19.40	39.21	31.13	31.13	

*Expansion of Mixtures of Alcohol and Water deduced from the observed Specific Gravities.*

Weight p.c. of Alcohol	Volume at 10°	Volume at 20°		Difference
		found	calculated	
0	100	100.154	100.154	
10	100	100.212	100.272	- 0.060
20	100	100.405	100.386	+ 0.019
30	100	100.632	100.489	0.143
40	100	100.783	100.601	0.182
45	100	100.827	100.652	0.175
50	100	100.808	100.700	0.168
59.77	100	100.914	100.789	0.125
69.70	100	100.980	100.874	0.106
79.81	100	101.020	100.954	0.066
89.89	100	101.052	101.034	0.018
100.00	100	101.088	101.088	

*Compressibility of Mixtures of Alcohol and Water for Pressure of One Atmosphere.*

Weight p.c. of Alcohol	Temperature	Compression		Difference
		observed	calculated	
0	9°	0.00004774	0.00004774	
10	11.2	0.00004351	0.00005387	- 0.00001036
20	11.5	0.00003911	0.00005998	0.00002087
30	10.2	0.00003902	0.00006584	0.00002682
40	9	0.00004347	0.00007118	0.00002771
45	8	0.00004608	0.00007364	0.00002756
50	9	0.00004878	0.00007600	0.00002722
59.77	10	0.00005620	0.00008029	0.00002409
69.70	10.1	0.00006159	0.00008426	0.00002267
79.81	9.6	0.00006942	0.00008775	0.00001833
89.89	11.1	0.00007950	0.00009140	0.00001190
100.00	9.7	0.00009349	0.00009349	

Determinations of the specific gravity of mixtures of alcohol and water at different temperatures have also been made by Mendelejeff (*Pogg. Ann.* cxxxviii. 103, 230), from which he infers that between the temperatures of 0° and 30°, the maximum of contraction takes place in mixtures corresponding with the formula  $C^2H^6O + 3H^2O$ .

Weight p.c. of Absolute Alcohol.	Specific Gravity, referred to Water at 4° = 100.000			
	at 0°	at 10°	at 20°	at 30°
0	99988	99975	99831	99579
5	99135	99113	98945	98680
10	98493	98409	98195	97892
15	97995	97816	97527	97142
20	97566	97263	96877	96413
25	97115	96672	96185	95628
30	96540	95998	95403	94751
35	95784	95174	94514	93813
40	94939	94255	93511	92787
45	93977	93254	92493	91710
50	92940	92182	91400	90577
55	91848	91074	90275	89456
60	90742	89944	89129	88304
65	89595	88790	87961	87125
70	88420	87613	86781	85925
75	87245	86427	85580	84719
80	86035	85151	84366	83463
85	84789	83967	83116	82232
90	83482	82665	81801	80918
95	82119	81291	80433	79553
100	80625	79788	78946	78096

The specific heats of mixtures of alcohol with water, carbon bisulphide, chloroform and benzene, have been determined by J. H. Schüller (*Pogg. Ann. Ergänzungsband*, v. 116, 192). The specific heats of these several liquids in the pure state were first determined with the following results:

Alcohol		Carbon Bisulphide		Chloroform		Benzene	
Temp.	Sp. Heat	Temp.	Sp. Heat	Temp.	Sp. Heat	Temp.	Sp. Heat
16-30°	0.6019	14-29.5°	0.2468	16-35°	0.2337	19.5-30.5°	0.4518
16-35°	0.6067			18-30°	0.2331	19.5-35.5°	0.4194
16-40.5°	0.6120					20-41°	0.4237

From the observed specific heats of absolute alcohol and benzene above given, the specific heats for other temperatures may be calculated by the formulae:

$$\text{for alcohol, } c = 0.5585 + 0.00093195 t + 0.0000003463 t^2$$

$$\text{for benzene, } c = 0.3798 + 0.00072 t$$

The specific heat of the carbon bisulphide actually used for the mixtures was 0.2442 for an interval of temperature 15° to 30°.

In the following tables,  $c$  denotes the observed specific heat of the mixtures,  $c_1$  the mean specific heat of the mixture calculated from those of its constituents:—

*Specific Heat of Mixtures of Alcohol and Water.*

Alcohol in 100 parts of Mixture	$c$	$c_1$	$\frac{c}{c_1}$
14.90	1.0391	0.9424	1.1026
20.00	1.0156	0.9227	1.1331
22.56	1.0136	0.9128	1.1433
28.56	1.0354	0.8896	1.1639
35.22	1.0076	0.8638	1.1665
44.35	0.9610	0.8285	1.1599
49.46	0.9162	0.8103	1.1307
49.93	0.9096	0.8061	1.1284
54.09	0.8826	0.7909	1.1159
54.45	0.8793	0.7895	1.1139
58.17	0.8590	0.7251	1.1082
73.90	0.7771	0.7172	1.0771
83.00	0.7168	0.6817	1.0515

*Specific Heat of Mixtures of Alcohol and Carbon Bisulphide.*

Alcohol in 100 parts of Mixture	$c$	$c_1$	$\frac{c}{c_1}$
16.04	0.3371	0.3016	1.1177
20.06	0.3560	0.3160	1.1266
30.06	0.3989	0.3517	1.1342
35.00	0.4133	0.3693	1.1164
40.53	0.4237	0.3881	1.0917
48.64	0.4471	0.4162	1.0742
59.30	0.4808	0.4564	1.0535
70.90	0.5138	0.4966	1.0346

*Specific Heat of Mixtures of Alcohol and Chloroform.*

Alcohol in 100 parts of Mixture	$c$	$c_1$	$\frac{c}{c_1}$
16.75	0.3348	0.2962	1.1303
28.77	0.3910	0.3410	1.1495
33.92	0.4130	0.4602	1.1466
39.78	0.4315	0.3821	1.1290
47.00	0.4539	0.4090	1.1098
56.46	0.4841	0.4443	1.0896
72.80	0.5331	0.5052	1.0552

*Specific Heat of Mixtures of Alcohol and Benzene.*

Alcohol in 100 parts of Mixture	c	c <sub>1</sub>	$\frac{c}{c_1}$
20.43	0.5022	0.4574	1.0979
24.45	0.5112	0.4646	1.1003
32.54	0.5268	0.4816	1.0939
48.74	0.5465	0.5139	1.0634
57.85	0.5565	0.5283	1.0534
66.89	0.5666	0.5455	1.0387
80.15	0.5862	0.5712	1.0271

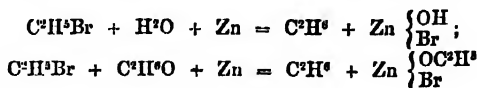
In all these alcoholic mixtures the observed specific heat is greater than the mean value obtained by calculation from the specific heats of the constituents, and it may even exceed the specific heat of that constituent which has the greater specific heat. As the proportion of alcohol becomes greater, the ratio of the true to the mean specific heat increases also, rapidly at first till it attains a maximum, then diminishes somewhat quickly at first, afterwards more slowly, and gradually approximates to the first value.

In the case of mixtures of alcohol and water, the excess of the observed over the calculated mean specific heat is confirmed by the experiments of Dupré and Page already cited, also by those of Jamin a. Amaury (*Compt. rend.* lxx. 1237), who explain it on the hypothesis that the specific heat of a body increases as its density diminishes, and must, therefore, be greater in a mixture in which each of the constituents is diffused through the entire volume.

**ETHYL BROMIDE**,  $C^2H^5Br$ . *Decomposition by the Copper-Zinc Couple* (p. 454).—The action of zinc coated by precipitation with finely divided copper on ethyl bromide at  $100^\circ$  is in the main similar to that which it exerts on the iodide (p. 479), giving rise to zinc ethylbromide,  $Zn \begin{Bmatrix} C^2H^5 \\ Br \end{Bmatrix}$  or  $Zn(C^2H^5)^2.ZnBr^2$ . It varies, however, greatly in different experiments, apparently depending on small differences in the conditions, the nature of which has not yet been determined; in some experiments no action took place, even when the ethyl bromide was heated with the dry couple for thirty-six hours. When the ethyl bromide is mixed with a little ethyl iodide, the reaction always takes place, and with comparative facility, the ethiodide at first formed appearing to facilitate the formation of the ethylbromide.

Zinc ethylbromide melts at  $62^\circ$  and crystallises on cooling in white pearly scales. When heated it yields zinc-ethyl, a great part of which, however, is decomposed, yielding ethane, ethylene, and metallic zinc,  $Zn(C^2H^5)^2 = Zn + C^2H^4 + C^2H^6$ , apparently in consequence of the high temperature required, so that the quantity of zinc-ethyl obtained is only about a third of that which is theoretically producible.

The action of the couple on ethyl bromide in presence of water or alcohol is very slow at ordinary temperatures, but proceeds much more rapidly on application of heat, ethane being evolved and bromhydrate or bromethylate of zinc remaining in the flask:—



(Gladstone a. Tribe, *Chem. Soc. J.* [2], xii. 410–415).

**Bromethyl bromide**,  $C^2H^4Br^2$  (obtained by the action of bromine on ethyl bromide at  $170^\circ$ ) treated with sodium ethylate yields sodium bromide and bromethylene (together with alcohol:  $C^2H^4Br^2 + C^2H^5NaO = NaBr + C^2H^5O + C^2H^4Br$ ).—The same products are obtained by the action of sodium ethylate on the addition-product of monobromethylene and dilute hydrobromic acid,  $C^2H^4Br.HBr$ , which agrees also in its other properties with bromethyl bromide, and is therefore probably identical therewith (Reboul, *Ann. Ch. Pharm.* clv. 29).

Ethyl bromide treated with bromine yields monobromethyl bromide  $C^2H^4Br.Br$ , ethylene bromide  $C^2H^4.Br^2$ , and dibromethyl bromide  $C^2H^5Br^2.Br$ . The two former may be separated by treatment with an alcoholic solution of potassium sulphhydrate, which converts the ethylene bromide into the compound  $C^2H^5S^2$ . **Monobromethyl bromide** treated with ammonia yields collidine,  $C^2H^4N$ , boiling at  $181^\circ$ . Monobromethyl bromide and potassium acetate, heated together in alcoholic solution, yield

aldehyde and acetal. Oxidation of monobromethyl bromide by means of lead dioxide and water, leads to the production of aldehyde.

*Dibromethyl bromide* may be produced by the action of bromine on ethylene bromide, and when the product thus obtained is treated with sodium ethylate, two substances having the composition  $C^2H^2Br^2$  are produced, one boiling at  $91^\circ$  the other at  $161^\circ$ . The products of the action of bromine on ethylene bromide contain a small proportion of a substance containing  $C^2H^2Br^1$ , and boiling, with partial decomposition, at  $209^\circ$ . This substance remains fluid at  $-20^\circ$ , but the isomeric body obtained by the action of bromine on acetylene forms crystals melting at  $185^\circ$  (Tawildarow, *Deut. Chem. Ges. Ber.* vi. 1459).

**ETHYL CHLORIDE,  $C^2H^5Cl$ .** The easiest method of preparing this compound is to pass hydrochloric acid gas into a boiling solution of zinc chloride in  $1\frac{1}{2}$  times its weight of alcohol of 95 p.c., contained in a flask connected with an inverted condenser and a wash-bottle containing water. Nearly the whole of the alcohol is thus converted into ethyl chloride (Groves, *Chem. Soc. J.* [2] xii. 637).

*Chlorinated Derivatives.*—It has hitherto been supposed that of the various bodies  $C^2H^4Cl^2$  produced by passing chlorine into ethyl chloride, only the final product  $C^2Cl^4$  is identical with the similarly composed product formed by the action of chlorine on ethylene chloride. According to Geuther a. Stapff, however (*Jenaische Zeitschrift*, vi. 228), this view is not correct, the two series from  $C^2H^2Cl^4$  (inclusive) to  $C^2Cl^4$  uniting into one. According to Regnault, the chlorination of ethyl chloride yields the bodies—

	$C^2H^4Cl^2$	$C^2H^3Cl^3$	$C^2H^2Cl^4$	$C^2HCl^5$
boiling at	$64^\circ$	$75^\circ$	$102^\circ$	$145^\circ$ .

On the other hand, according to Geuther, the action of chlorine on chloride of ethylene yields the compounds—

	$C^2H^4Cl^2$	$C^2H^3Cl^3$	$C^2H^2Cl^4$	$C^2Cl^4$
boiling at	$82.5^\circ$	$116^\circ$	$135^\circ$	$153.5^\circ$ .

Geuther a. Stapff, by fractionally distilling a large quantity of crude chlorinated ethyl chloride (the portions boiling at  $62^\circ$ – $72^\circ$  and at  $75^\circ$  being subjected, after further chlorination, to the same treatment) obtained, of products not further alterable by fractionation, and in addition to the constantly occurring  $C^2Cl^4$ , only bodies boiling respectively at:

II.	IIa.	III.	IIIa.	IV.	V.
$58^\circ$ – $64^\circ$	$81^\circ$ – $84^\circ$	$75^\circ$	$115^\circ$	$135^\circ$	$153^\circ$ .

The portion which originally passed over at  $102^\circ$  or  $146^\circ$ , always split up into bodies of this series (and  $C^2Cl^4$ ). A portion of III a. boiling at  $115.6^\circ$  (corr.), gave, on analysis, numbers agreeing with the formula  $C^2H^2Cl^4$ . The product II a. was obtained, in small quantity only, by very careful fractional distillation of a product boiling between  $75^\circ$  and  $100^\circ$ ; it exhibited the composition of a mixture of  $C^2H^4Cl^2$  and  $C^2H^3Cl^3$ . If, then, we admit with Geuther that in the group  $C^2H^2Cl^4$ —equality of boiling point and elementary composition indicate chemical identity, the preceding facts must be regarded as establishing the proposition above stated, viz., that the corresponding bodies produced by chlorination of ethyl chloride and of ethylene chloride belong to the same series. According to Stapff, the body above designated as II. yields, by further distillation, a liquid having exactly the composition  $C^2H^4Cl^2$ , and boiling between  $57^\circ$  and  $59^\circ$ ; identical, therefore, with ethylidene chloride.

Stadel, by submitting 5000 grams of the crude product of the action of chlorine on ethyl chloride to a very large number of fractional distillations, found that ultimately only 3 or 4 grams were obtainable boiling between  $80^\circ$  and  $90^\circ$ ; whence he infers that ethylene chloride does not occur amongst the products of the reaction, the small quantity which Geuther obtained being probably formed—as, indeed, Geuther also supposes—from alcohol contained in the ethyl chloride. Small quantities of pure mono- and di-chlorinated ethyl chloride were separated, boiling respectively at  $62^\circ$  and  $74.6^\circ$ .

Regnault found the boiling point of monochlorethyl chloride (ethylidene chloride,  $ClP.ClHCl^2$ ) to be  $64^\circ$ , Geuther  $57^\circ$ – $59^\circ$ , Beilstein, and also Krämer,  $60^\circ$ . Of these results Krämer's is perhaps the most trustworthy, as he operated on larger quantities of liquid.

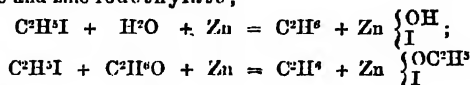
**ETHYL IODIDE,  $C^2H^5I$ .** This compound, treated with *sulphuric anhydride*, yields, with separation of iodine, an acid isomeric with ethyl-sulphuric acid, ( $C^2H^5$ )  $HSO^4$ . *Sulphuric chlorhydrate*,  $SO^2(HO)Cl$ , acts strongly on ethyl iodide, converting it into ethyl-sulphuric acid (Wroblewsky, *Zeitschr. f. Chem.* [2], iv. 563; v. 280).

When a solution of *phosphine* in ethyl iodide is heated, either alone or mixed with an ethereal solution of zinc iodide, the iodides of triethyl- and tetraethyl-phosphonium are produced (Hofmann, *Deut. Chem. Ges. Ber.* iv. 372).

**Decomposition by the Copper-Zinc Couple.**—Zinc-foil coated with metallic copper by immersing it in a 1 p.c. solution of cupric sulphate, decomposes ethyl iodide at 100°, yielding white crystalline ethiodide of zinc,  $\text{Zn}(\text{C}^2\text{H}^5)_2\text{I}$  or  $\text{Zn}(\text{C}^2\text{H}^5)_2\cdot\text{ZnI}_2$ , which, when gently heated, is resolved into zinc-ethyl and zinc iodide, together with more or less of combustible gas consisting of ethane and ethylene, resulting from decomposition of the ethyl. The reaction is, in fact, the same as that which takes place when ethyl iodide is strongly heated with zinc alone in sealed tubes (ii. 524). At ordinary temperatures, or at 100°, pure zinc has no action on ethyl iodide. The ethiodide of zinc is resolved by gentle heating into zinc iodide and zinc-ethyl,  $\text{Zn}(\text{C}^2\text{H}^5)_2$ , the quantity of the latter obtained being about two-thirds of the total quantity theoretically producible from the materials employed; this reaction affords, therefore, an easy method of obtaining zinc-ethyl in considerable quantity.

Ethiodide of zinc may be viewed either as  $\text{Zn} \begin{Bmatrix} \text{C}^2\text{H}^5 \\ \text{I} \end{Bmatrix}$ , formed by direct combination, or as a compound of zinc-ethyl with zinc iodide,  $\text{Zn}(\text{C}^2\text{H}^5)_2\cdot\text{ZnI}_2$ . The latter view is perhaps the more probable, inasmuch as the especial function of a galvanic couple appears to be the resolution of a binary compound into its elements.

When the couple acts on ethyl iodide in presence of water, ethane is abundantly given off, and zinc iodhydrate remains in the flask; in presence of alcohol the products are ethane and zinc iodethylate;

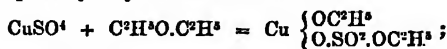


(Gladstone & Tribe, *Chem. Soc. J.* [2], xi. 445).

**ETHYL OXIDE** or **ETHYLIC ETHER**  $(\text{C}^2\text{H}^5)_2\text{O}$ . Pure ether, when shaken with water, does not communicate to the water anything capable of yielding the iodoform reaction (indicating the presence of alcohol) when treated with iodine and potash; such ether can be obtained by distilling purified ether two or three times over sodium, the entrance of moisture being prevented by means of a chloride of calcium tube. Ether thus purified does not give the iodoform reaction even after standing  $1\frac{1}{2}$  year in well closed vessels; if, however, it be mixed with water or dilute sulphuric acid, and heated to 100° for a day, a strong iodoform reaction is obtained, and when it is kept in contact with water at the ordinary temperature for three or four months, the same result ensues.

Pure ether sealed up with fragments of sodium, caustic potash, or potassium carbonate, was unaffected even after many months; but in contact with calcium chloride, sodium chloride, or copper sulphate (anhydrous), decomposition took place, and a body which yielded the iodoform reaction was produced.

It appears therefore that bases do not cause this change in ether, while neutral salts and acids do; possibly ethylates are formed thus:



or possibly the ether splits into alcohol and ethylene (Lieben, *Ann. Ch. Pharm.* clxv. 134).

On the formation of alcohol from ether, and of ether from alcohol, by the action of water and dilute sulphuric acid, see p. 473.

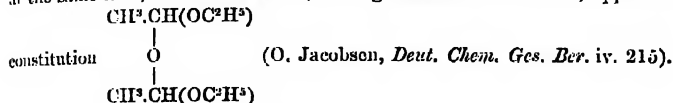
**Action of Ether on Iodides.**—When a concentrated solution of an iodide is mixed with starch-paste and then shaken with ether, part of the iodine is separated, and the starch is turned blue. If the solution is dilute, the blueing does not appear till after two or three hours, and in extremely dilute solutions not till after two or three days. On filtering from the blue starch and adding more ether, a blue colour is again produced, and so on, till at length all the iodine is removed from the compound. Mineral waters containing iodides exhibit, when thus treated, the same reactions as artificially prepared solutions (E. Ferriero, *J. Pharm. Chim.* [4], xvi. 107).

#### Chlorinated Derivatives of Ethyl Oxide.

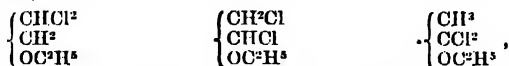
**Monochloretethyl oxide**,  $\text{C}^4\text{H}^9\text{ClO}$ , the first product of the action of chlorine on ether, is identical with the body which Wurtz & Frapollé obtained (i. 3, 107) by the action of hydrochloric acid on an alcoholic solution of aldehyde. Pure monochlor-



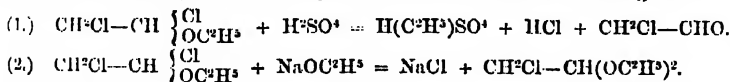
ethyl oxide boils at  $97^{\circ}$ – $98^{\circ}$ . With sodium ethylate it forms acetal; sulphuric acid decomposes it, with formation of ethyl-sulphuric acid, hydrochloric acid, and aldehyde. These reactions show that its constitutional formula is  $\text{CH}_3\text{CH} \begin{Bmatrix} \text{Cl} \\ \text{OC}^2\text{H}^3 \end{Bmatrix}$ . When treated with water it yields, besides hydrochloric acid, a liquid which boils a little below  $50^{\circ}$ , has the composition  $\text{CH}_3\text{CH} \begin{Bmatrix} \text{OH} \\ \text{OC}^2\text{H}^3 \end{Bmatrix}$ , and from its analogy to chloral alcoholate may be called aldehyde alcoholate. Condensation-products are formed at the same time, the first of which, boiling between  $80^{\circ}$  and  $84^{\circ}$ , appears to have the



**Dichlorethyl Oxide**,  $\text{C}^2\text{H}^3\text{Cl}_2\text{O}$  (Jacobsen, *loc. cit.*; Abeljanz, *Ann. Chem. Pharm.* xiv. 197). Lieben has shown that both the chlorine-atoms of this compound are situated in one ethyl group, as represented by the formula  $\text{C}^2\text{H}^3\text{Cl}_2\text{OC}^2\text{H}^3$  (1st Suppl. 596); but he has not determined which of the three following formulæ, included in the preceding, viz.,

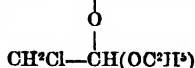


must be accepted as the true representative of its constitution, though, for a reason to be mentioned hereafter, he gives the preference to the third. But the reaction of the compound with sulphuric acid, by which it is easily and completely resolved into ethyl-sulphuric acid, hydrochloric acid, and monochloraldehyde,  $\text{CH}^2\text{Cl}\cdot\text{CHO}$ , and with sodium ethylate, whereby it is converted into monochloroacetal,  $\text{CH}^2\text{Cl}\cdot\text{CH}(\text{OC}^2\text{H}^3)^2$ , identical with Lieben's ethylchlorinated ethyl oxide (1st Suppl. 597) show that it is correctly represented by the second of the formulæ above given:—



By the action of water, dichlorethyl oxide is converted into the alcoholate of monochloraldehyde,  $\text{CH}^2\text{Cl}-\text{CH} \begin{Bmatrix} \text{OC}^2\text{H}^3 \\ \text{OH} \end{Bmatrix}$ , boiling at  $95^{\circ}$ – $96^{\circ}$ , together with condensation-products (especially on warming), the first of which distils at about

$165^{\circ}$ , and has the composition



This body is analogous to Ginsky's monochloraldehyde hydrate,  $\text{C}^2\text{H}^3\text{ClO} + \frac{1}{2}\text{H}^2\text{O}$ , or  $\text{C}^2\text{H}^3\text{ClO}^2 + \text{H}^2\text{O}$  (Deut. Chem. Ges. Ber. iii. 870), the constitution of which



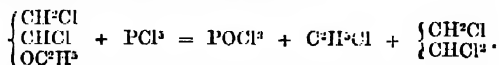
The formula of dichlorethyl oxide deduced from the preceding reactions is corroborated by the experiments of Abeljanz on the action of phosphorus trichloride on this compound.

The two substances brought together in molecular proportion react pretty briskly, the temperature rising to  $65^{\circ}$  or  $70^{\circ}$ . The experiment was performed in a retort connected with an upright condenser, and this again with a series of Woulfe's bottles, leading finally to a well-cooled Liebig's condenser, terminating in a U-tube surrounded by ice and salt. A small quantity of hydrochloric acid was collected in the Woulfe's bottles, and in the U-tube a considerable amount of pure ethyl chloride. The residue contained phosphorus trichloride and oxychloride, and when submitted to distillation gave, below  $130^{\circ}$ , a liquid which, when treated with water, yielded a large quantity of hydrochloric acid and a solution having a peculiar aldehydic smell. To isolate this aldehydic body, the solution was neutralised by boiling with lead oxide, and distilled. A colourless oil was deposited from the distillate, but as it was decomposed by redistillation, the whole was oxidised by heating it with excess of silver oxide. After

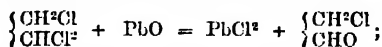
removal of the reduced silver and the silver chloride, which had been simultaneously produced, the acid was converted into zinc salt and analysed. The physical properties and composition of this compound showed that it was zinc glycolate,  $\text{Zn}(\text{C}^2\text{H}^2\text{O}^2)^2$ .

The products of the action of phosphorus pentachloride boiling above  $130^\circ$  consisted chiefly of unchanged dichlorethyl oxide.

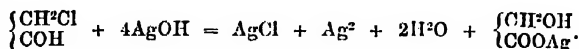
The principal reaction between phosphorus pentachloride and dichlorethyl oxide may be represented by the following equation:—



The last body, by boiling with lead oxide, yields monochloraldehyde:—



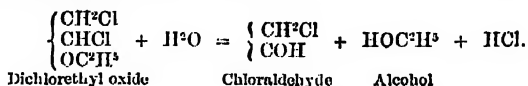
and this, when oxidised by silver oxide, gives silver chloride, metallic silver, and silver glycolate:—



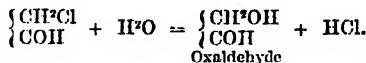
*Reaction of Dichlorethyl Oxide with Water and with Alkalis.*—Dichlorethyl oxide heated in sealed tubes, with seven or eight times its volume of water, to  $115^\circ$ – $120^\circ$ , but not higher, gives a colourless homogeneous solution containing hydrochloric acid, ethyl alcohol, and a mixture of aldehydes, among which chloraldehyde may be identified by treating it with silver oxide, whereby it is converted into glycollic acid. Another portion of the watery solution of the aldehyde, exposed for a week to the air and then evaporated, yielded a mixture of two kinds of crystals which, when separated and recrystallised, proved to be monochloroacetic acid (from the chloraldehyde) and glycollic acid. The latter could only have resulted from the oxidation of the hitherto unknown oxaldehyde,  $\left\{ \begin{array}{l} \text{CH}^2\text{OH} \\ \text{CHO} \end{array} \right\}$ , which may be regarded as the aldehyde of glycollic acid.

The oily body which was produced in small quantity by distillation of the original acid solution, is probably a hydroxyl-chlorethyl oxide,  $\left\{ \begin{array}{l} \text{C}^2\text{H}^2\text{Cl}(\text{OH}) \\ \text{O.C}^2\text{H}^2 \end{array} \right\}$ .

From these results the principal reaction between water and dichlorethyl oxide may be represented as follows:—

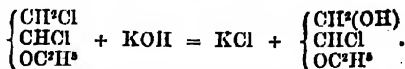


The oxaldehyde results from the subsequent decomposition of the chloraldehyde by water:—

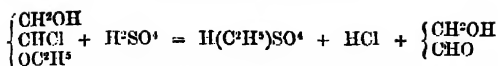


With *alkalis* dichlorethyl oxide yields products similar to those obtained in its decomposition by water, viz., alcohol, chloraldehyde, and two other chlorinated bodies. One of these has the composition of a hydroxyl-chlorethyl oxide,  $\left\{ \begin{array}{l} \text{CH}^2\text{Cl} \\ \text{CH}(\text{OH})(\text{OC}^2\text{H}^2) \end{array} \right\}$ , and boils at about  $153^\circ$ ; the other is a condensation-product,  $\left\{ \begin{array}{l} \text{C}^2\text{H}^2\text{Cl}.\text{OC}^2\text{H}^2 \\ \text{O} \end{array} \right\}$ , boiling at  $163^\circ$ – $165^\circ$ , and identical with the body observed by Jacobson as a product of the decomposition of dichlorethyl oxide with water.

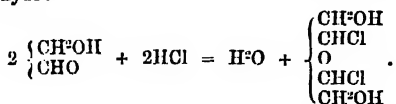
Besides the reaction in which the hydroxyl-chlorethyl oxide, just described, is the principal product, another which yields an isomeric of that body occurs at the same time, viz.:—



This latter substance is not susceptible of condensation, but when treated with concentrated sulphuric acid, it yields hydrochloric acid, ethyl-sulphuric acid, and oxaldehyde:—



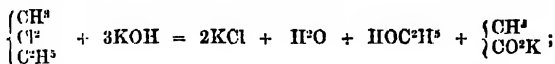
together with a small quantity of a body,  $\text{C}^2\text{H}^3\text{Cl}^2\text{O}^2$ , which is the analogue of ethylidene oxychloride, and results from a secondary reaction between the hydrochloric acid and the oxaldehyde:—



The condensation-product,  $\text{C}^2\text{H}^{14}\text{Cl}^2\text{O}^2$ , obtained from dichlorethyl oxide by the action of potash, gives scarcely any hydrochloric acid when treated with sulphuric acid, but forms chloraldehyde, water, and ethylsulphuric acid.

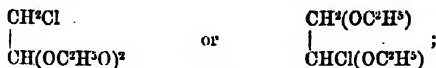
The chloraldehyde cannot be purified by fractional distillation, but when oxidised by silver oxide it gives glycollic acid; on exposure to the air it leaves crystals of monochloroacetic acid. It unites with bisulphite of soda, and ammonia passed into its ethereal solution produces a compound which crystallises in large pearly tables melting at about  $136^\circ$ .

Lieben, by treating dichlorethyl oxide with potash, obtained indications of the formation of acetic acid, a result which would imply that dichlorethyl oxide should be represented by the third of the preceding formulæ,  $\text{CH}^2\text{Cl}^2.\text{OC}^2\text{H}^3$ ; thus —



or at all events that this modification was present in the substance operated on. But if this were the case, acetic acid should also have been found in the final product of the series of reactions described by Abeljan, who prepared his dichlorethyl oxide exactly according to Lieben's directions, but not a trace of acetic acid could be discovered. Neither could acetic acid be detected in the saline residue obtained by the action of potash on dichlorethyl oxide, that residue consisting of potassium chloride with a small quantity of formate.

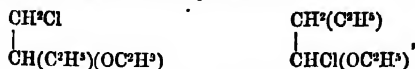
Dichlorethyl oxide being then represented by the formula  $\begin{Bmatrix} \text{CH}^2\text{Cl} \\ \text{CHCl}.\text{OC}^2\text{H}^3 \end{Bmatrix}$ , the compounds formed from it by the action of sodium-ethylate, zinc-ethyl, &c. (*1st Suppl.* 597) must be represented by analogous formulæ, viz. oxethyl-chlorethyl oxide  $\text{C}^2\text{H}^3\text{Cl}^2\text{O}^2$ , the first product of the action of sodium ethylate, by either of the formulæ



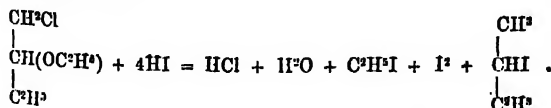
and dioxethyl-ethyl oxide,  $\text{C}^2\text{H}^{12}\text{O}^2$ , the product obtained by the further action of the same reagent, by the formula



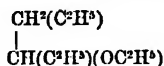
Ethylchloroethyl oxide,  $\text{C}^4\text{H}^{13}\text{ClO}$ , the first product of the action of zinc-ethyl on dichlorethyl oxide, may be represented by either of the formulæ



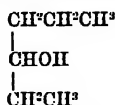
more probably however by the former, which is in accordance with the transformation of this compound into secondary butyl iodide or methyl-ethyl-carbonyl iodide by the action of hydriodic acid:



Diethylated ethyl oxide,  $\text{C}^6\text{H}^{16}\text{O}$ , the second product of the action of zinc-ethyl on dichlorethyl oxide, has the constitution

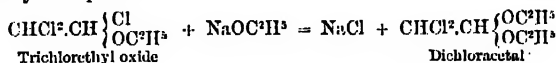


and the hexyl alcohol obtained by treating it with hydriodic acid and saponifying the resulting iodide, is represented by the formula

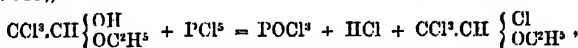


that is to say, it is ethyl-butyl carbinol.

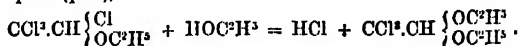
**Trichlorethyl Oxide**,  $\text{C}_2\text{H}_3\text{Cl}_3\text{O}$ , is also formed by the action of chlorine on ether, but it cannot be separated in the pure state by fractional distillation, dichlorethyl oxide being the most highly chlorinated product that distills unchanged. The presence of the trichlorinated ether may however be proved indirectly, namely, by the action of sodium ethylate on the residue obtained in the distillation of the crude dichlorethyl oxide after the temperature has risen above  $155^\circ$ . A mixture of chlorinated acetals is thus obtained, which, when submitted to fractional distillation, yields moderately pure dichloroacetal. This reaction establishes the constitution of trichlorethyl oxide, as shown by the equation



**Tetrachlorethyl Oxide**,  $\text{C}_2\text{H}_2\text{Cl}_4\text{O}$  =  $\text{CCl}^2\text{CH} \begin{Bmatrix} \text{Cl} \\ \text{OC}^2\text{H}^5 \end{Bmatrix}$ . This compound, prepared by the action of phosphorus pentachloride on chloral alcoholate (Henry's process, p. 313),



boils at  $189.7^\circ$  under the pressure of (reduced to  $0^\circ$ ) 857.5 mm. and has a density of 1.4370 at  $0^\circ$ , 1.4182 at  $15.2^\circ$ , 1.3055 at  $99.9^\circ$ . Heated with alcohol for several hours in a bath of salt water, it yields the trichloroacetal,  $\text{CCl}^2\text{CH} \begin{Bmatrix} \text{OC}^2\text{H}^5 \\ \text{OC}^2\text{H}^5 \end{Bmatrix}$ , discovered by Wurtz a. Frapolli (p. 2),



The same transformation is effected, though less sharply, by sodium ethylate, or by a very strong alcoholic solution of potash. If, however, the tetrachlorinated ether be treated with a 10 p.c. solution of potassium hydrate in absolute alcohol, a totally different reaction takes place, a molecule of hydrochloric acid being eliminated, and a compound formed, which appears to have the composition  $\text{CCl}^2 = \text{CCl} - \text{OC}^2\text{H}^5$  (Paternò a. Pisati, *Gazzetta chimica italiana*, ii. 333).

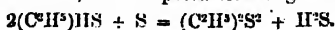
Tetrachlorethyl oxide is likewise formed, together with lower chlorinated products, by the action of chlorine on ether at  $90^\circ$ . If the action be not pushed too far, a liquid is obtained which, when treated with sulphuric acid, yields a considerable quantity of chloral  $\text{CCl}^2\text{CHO}$ , and therefore contains trichlorethyl oxide (Jacobsen).

**Pentachlorethyl Oxide**,  $\text{C}_2\text{HCl}_5\text{O}$ , is the end-product of the action of chlorine on ethyl oxide in diffused daylight. It is a rather thick colourless liquid of sp. gr. 1.646. Its reactions show that it still retains one of the ethyl-groups of ethylic oxide intact, and therefore that its constitution is represented by the formula  $\text{CCl}^2\text{OC}^2\text{H}^5$  ( $\text{OC}^2\text{H}^5$ ).

To extend the chlorination to the second ethyl group, the influence of sunshine is necessary. In that case, perchlorinated ether  $\text{C}_2\text{Cl}_6\text{O} = \text{CCl}^3\text{CCl}^3\text{O} \cdot \text{CCl}^3\text{CCl}^3$  is produced (ii. 541).

The order in which the hydrogen atoms in the first ethyl group are successively replaced by chlorine, may be represented by the formula  $\text{CH}_3\text{H} \cdot \text{CH}_2\text{H} \cdot \text{O} \cdot \text{CCl}^3$  2, 3, 4, 1, 5 (Jacobsen, *loc. cit.*)

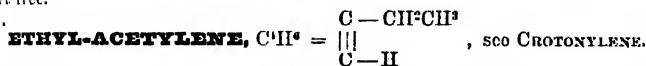
**ETHYL SULPHIDES.** (M. Müller, *J. pr. Chem.* [2], iv. 89). Mercaptan heated in a sealed tube for six hours to  $150^\circ$  with sulphur in the proportion of 2 molecules to 1 atom of the latter, is decomposed according to the equation,—



*Selenium* is without action on mercaptan. Ethyl monosulphide,  $(C^2H^5)^2S$ , is entirely unacted on by sulphur, and may, when mixed with mercaptan, be readily obtained pure, by heating the mixture with sulphur, whereby the mercaptan is converted into ethyl bisulphide and hydrogen sulphide.

Ethyl disulphide,  $(C^2H^5)^2S_2$ , heated with sulphur, yields the trisulphide  $(C^2H^5)^2S_3$ , as a yellow oil, heavier than water, which cannot be distilled alone but may be obtained pure by slowly distilling it in a current of steam. This compound may also be prepared by distilling liver of sulphur and potassium sulphovinate from a retort, with frequent addition of water, so long as oily drops pass over. The oil thus obtained is a mixture of ethyl di- and tri-sulphides, and to convert it entirely into the latter, it is heated with sulphur in sealed tubes for some hours at  $150^\circ$ . The contents of the tubes are then carefully distilled in a current of steam.

On shaking ethyl trisulphide with *mercury*, the third sulphur-atom is slowly removed; also on heating with copper turnings in a sealed tube to  $150^\circ$  for a day. When the product is suspended in water and carefully oxidised by fuming nitric acid, an amount of sulphuric acid is produced exactly equivalent to the third sulphur-atom, two molecules of ethylsulphurous acid being formed at the same time. The above-mentioned mixture of di- and tri-sulphides may therefore be employed with advantage for the preparation of ethylsulphurous acid,  $C^2H^5 \cdot SO_2 \cdot OH$ . *Aqueous potash*, shaken for a long time with ethyl trisulphide, removes the third sulphur-atom; alcoholic potash seems to act differently. The trisulphide heated with potassium cyanide yields potassium sulphocyanate and ethyl disulphide. Many *metallic salts* remove the third sulphur atom, with simultaneous formation of metallic sulphide. *Silver oxide* forms silver sulphide and ethylsulphurous acid; *silver acetate* acts similarly, acetic acid being set free.

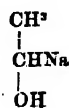
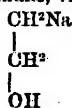
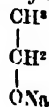


**ETHYLAMINES.** The volatile by-products rich in ethyl chloride, obtained in the manufacture of chloral, have been applied by A. W. Hofmann (*Deut. Chem. Ges. Ber.* 1870, 109 and 776) to the preparation of ethyl-bases on the large scale. These products are heated to  $100^\circ$  for an hour in a wrought-iron digester with three times their volume of 95 p.c. alcohol previously saturated with ammonia at  $0^\circ$ ; the liquid is filtered from the separated sal-ammoniac; the alcohol distilled off; and the residue evaporated to dryness. This residue, which contains the hydrochlorides of the three ethyl-bases, is decomposed by a concentrated solution of caustic soda, and the bases which separate are removed and separated from one another by treatment with oxalic ether (ii. 551). With reference to this method of separation, Hofmann observes that the diethyloxamide and ethylic diethyloxamate must be separated by filtration at  $0^\circ$ , and not by treatment with hot water, since ethylic diethyloxamate is resolved by boiling with water into alcohol and diethyloxamic acid. The chief product of the action of ammonia on ethyl chloride is diethylamine.

*Tetreethylammonium bromide*,  $(C^2H^5)^4NBr$ , unites very easily with bromine, forming polybromides, among which the tribromide is the most stable. When an aqueous solution of tetreethylammonium bromide is mixed with bromine-water, a light red-precipitate of the tribromide is immediately formed, which, on further addition of bromine, turns crimson-red and is converted into the pentabromide. The latter, however, on exposure to the air, gives off 1 mol. bromine, and is reconverted into the tribromide. The same result is obtained when alcohol or chloroform is used as the solvent, the red crystalline mass which separates quickly losing bromine, and yielding the tribromide.

*Tetreethylammonium tribromide*,  $(C^2H^5)^3NBBr_2$ , crystallises from alcohol in beautiful light orange-red needles which melt at  $78^\circ$ . It dissolves easily in alcohol and carbon sulphide; in chloroform only in certain proportions, an excess of chloroform floating in the solution without becoming coloured. On mixing a saturated alcoholic solution of the tribromide with an alcoholic solution of iodine, small crystals, resembling iodine, and probably consisting of the tri-iodide, separate at first, together with the tribromide. On adding a solution of iodine in potassium iodide to the alcoholic solution of the tribromide, a brown precipitate is formed consisting of the tri-iodide  $(C^2H^5)^3NI_3$ . (Clamor-Marquart, *J. pr. Chem.* [2], i. 429).

**ETHYLATE OF SODIUM**,  $C^2H^5ONa$ . The constitution of this compound may be represented by three different formulæ, viz:



If the first formula be the true one, the action of ethyl iodide on sodium ethylate ought to yield ethyl oxide,  $C^2H^5-O-C^2H^5$ ; if the second is correct, normal butylic alcohol,  $CH^3CH^2CH^2-CH^2OH$ , should be obtained; and finally, if the third formula correctly expresses the constitution of sodium ethylate, the action of ethyl iodide on it should give secondary butylic alcohol,  $CH^3-CH(C^2H^5)-OH$ .

Now the action of ethyl iodide on sodium ethylate is well known to yield ethyl oxide, and according to Laubenheimer (*Ann. Ch. Pharm.* clxiv. 280), it yields nothing else, excepting a small quantity of ethylene, probably arising from a secondary reaction according to the equation,

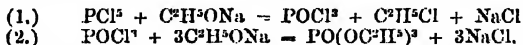


This action is analogous to the decomposition of ethyl iodide by sodium hydrate, and to the formation of butylene by the action of alcoholic potash on butyl iodide.

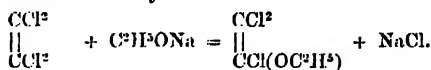
From these results Laubenheimer concludes that the true formula of sodium ethylate is  $C^2H^5ONa$ , and not  $C^2H^5Na.OIL$ , as proposed by Wanklyn (*1st Suppl.* 244, 1028).

*Reactions of Sodium Ethylate with Chlorides.*—Geuther u. Brockhoff (*Jenaische Zeitschrift*, vii. 359).

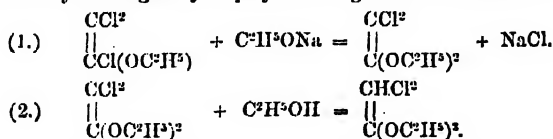
1. With phosphorus pentachloride. When 4 mol. sodium ethylate are acted on by 1 mol.  $PCl^5$ , the products obtained are triethylie phosphate, ethyl chloride, and sodium chloride, together with a little alcohol, the reaction probably taking place in two stages, thus:



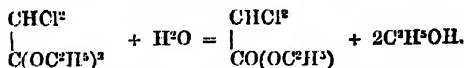
2. With perchlorethylene  $C^2Cl^4$ .—The action of sodium ethylate on perchlorethylene has been studied by Fischer and Geuther, who found that, besides sodium chloride, sodium ethylglyoxalate, and ethyl dichloracetate, there were also produced two substances having the composition  $C^2H^5Cl^2O$  and  $C^2H^5Cl^2O^2$ . These substances have since been proved to be trichlorethoxyl-ethylene and triethylie dichloracetate. Geuther u. Brockhoff consider that trichlorethoxyl-ethylene is the primary product of the reaction, and that it is derived from perchlorethylene by the replacement of one atom of chlorine by one atom of ethoxyl:—



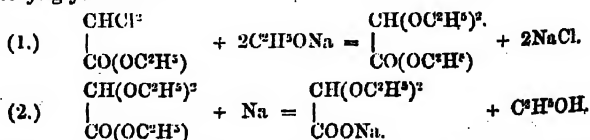
The triethylie dichloracetate may be derived from the above compound as follows, the sodium ethylate originally employed having contained alcohol:



The ethyl dichloracetate may arise from the action of water on tribasic ethyl dichloracetate, the water being partly hygroscopic and partly derived from secondary reactions:



The action of sodium ethylate on this ether gives rise to ethyl diethylglyoxalate, this compound being subsequently decomposed by sodium hydrate into alcohol and sodium diethyl-glyoxalate:

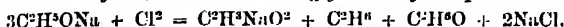


The above-mentioned intermediate reactions were confirmed by experiments in which the action of the sodium ethylate was to some extent limited.

The action of sodium ethylate free from alcohol on perchlorethylene gave rise to the products enumerated above, but in smaller quantities, also to a gas burning with a blue flame, and some brown products.

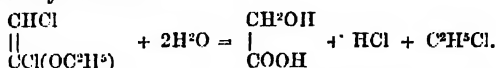
3. With perchlorethane  $C^2Cl^4$ .—When an ethereal solution of perchlorethane.

was heated to  $106^{\circ}$ – $110^{\circ}$  with sodium ethylate, an energetic action took place, ethane being evolved as a gas burning with a non-luminous flame. On distilling the products of the reaction, perchlorethylene was found in the distillate, accompanied, as might be expected, by those substances which are formed by the action of sodium ethylate on it. Besides sodium chloride and resinous substances, the residue contained sodium ethylglyoxalate and sodium acetate. The latter appears to be formed by the action of chlorine on sodium ethylate, the chlorine being yielded by the perchlorethane:



4. With trichlorethylene chloride  $\text{C}^2\text{HCl}_3$ .—These substances act readily on one another, perchlorethylene being produced. Similar results were obtained when the trichlorethylene chloride was dissolved in ether and then treated with sodium ethylate.

5. With dichlorethylene chloride.—This chloride was digested for some time with sufficient alcoholic sodium ethylate to replace all the chlorine by ethoxyl. The product was then distilled, and by the addition of water to the distillate, an oil was obtained which had the composition of dichloroethoxyl-ethylene,  $\text{C}^2\text{HCl}(\text{OC}^2\text{H}^5)$ . This substance is a colourless liquid having a peculiar aromatic odour. It boils at  $128.2$  (corr.), and has a specific gravity of  $1.08$  at  $10^{\circ}$ . Moisture acts slowly on it, hydrochloric acid and ethyl chloride being formed. Heated in a sealed tube to  $180^{\circ}$  with excess of water, it is entirely decomposed, with formation of glycollic acid, hydrochloric acid, and ethyl chloride:



Excess of alcoholic sodium ethylate converts dichloroethoxyl-ethylene into the sodium salt of ethyl-glycollic acid, ethyl monochloracetate being probably formed as an intermediate product. A small quantity of the latter was apparently formed during the action of sodium ethylate on dichlorethylene chloride, and it may be also formed, together with ethyl chloride, by the action of sodium ethylate on excess of dichloroethoxyl-ethylene.

6. With monochlorethylene chloride  $\text{C}^2\text{H}^2\text{ClCl}^2$ .—When this chloride is treated with excess of sodium ethylate, an action takes place, resulting in the formation of dichlorethylene and a small quantity of sodium acetate.

7. With perchloromethane  $\text{C}^2\text{Cl}_4$ .—One molecule of this compound was diluted with two volumes of ether and treated with 4 molecules of sodium ethylate, the whole being then digested for about 4 hours under a slightly increased pressure. After the reaction, during which no gas was evolved, had terminated, the product was distilled, and the distillate was found not to contain any portion boiling above  $75^{\circ}$ . The residue in the retort contained a brown substance insoluble in water, which, after washing with hydrochloric acid, contained 63.6 p.c. of carbon, and 72 p.c. of hydrogen. This substance contained no chlorine and yielded no ash.

The alkaline liquor obtained by heating the residue with water yielded, when treated with hydrochloric acid, a brown resinous precipitate, soluble in alkalis and alcohol. It contained 60.8 p.c. C., and 6.2 p.c. H. The alkaline liquor also contained traces of carbonic acid and oxalic acid.

On the reaction of sodium ethylate with *acetamide*, see page 3

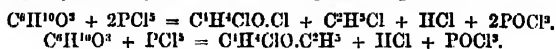
**ETHYLCYANOPHOSPHIDE.** See CYANETHYL-PHOSPHIDE (p. 405).

**ETHYL-DIACETIC ACID**,  $\text{C}^6\text{H}^{10}\text{O}^2$  (Genther, *Jenaische Zeitschrift*, vi. 560, 575; *J. pr. Chem.* [2], iv. 431, 450). In preparing the sodium salt of this acid by the action of sodium on ethyl-acetate (1st Suppl. 601), Genther recommends the use of a large excess of the acetic ether, so that all the sodium may dissolve without any great rise of temperature, which would cause the formation of resinous products, dehydracetic acid, &c. By using 4 pounds of ethyl acetate to 60 grains of sodium, he obtained 165 grams of ethyl-diacetic acid corresponding very nearly with the theoretical amount.

*Action of Phosphorus Pentachloride.*—When the pentachloride (33 parts) is gradually added to ethyl-diacetic acid (10 parts) it dissolves without much evolution of heat, forming a reddish brown liquid; at the same time large quantities of hydrogen chloride and ethyl chloride are evolved, but no acetyl chloride. The product, which consists of phosphorus oxychloride and the chlorides of several acids, cannot be separated by fractional distillation, and must therefore be gradually added to water kept at a low temperature, in which it readily dissolves. On distilling the aqueous solution, there passes over at first, with the vapour of water, an oil which does not solidify; then a milky liquid which deposits crystals on cooling, after which the distillate becomes clear. The milky liquid contains the monochlorinated derivative of liquid crotonic acid; called by

Gauthier quartenylic acid; the residue in the retort contains the corresponding derivative of solid crotonic acid (Gauthier's tetraerylic acid: *1st Suppl.* 511); and the neutral oil is a mixture of the ethylic ethers of these two chlorinated acids.

Hence it appears that the action of phosphorus pentachloride on ethyl-di-acetic acid gives rise to the chlorides of the two modifications of monochlorocrotonyl,  $C^2H^3ClO$ , and the ethers of the corresponding acids, together with ethyl chloride, hydrogen chloride, and phosphorus oxychloride; according to the equations:

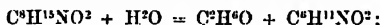


*Action of Ammonia on Ethylic Ethyl-di-acetate.* The action of concentrated ammonia on this ether at ordinary temperatures gives rise to two compounds, a soluble amide,  $C^2H^{10}NO^2$ , which is the amide of ethyl-di-acetic acid,  $C^2H^3O^2.NH^3$ , and an insoluble amide,  $C^2H^{10}NO^2$ , which might be regarded either as the amide of diethyl-di-acetic acid  $C^2H^{10}O^2.NH^3$ , or as the ethylamide of ethyl-di-acetic acid  $C^2H^3O^2.NH(C^2H^3)$ .

The insoluble amide is decomposed by moisture, and more quickly by acids, ammonia being liberated and the crystals being converted into an oily liquid which is nearly pure ethylic ethyl-di-acetate, whence it may be inferred that the insoluble amide is the ethyl amide of ethyl-di-acetic acid:



When the insoluble amide is heated with water to  $100^\circ$  in a sealed tube for several days, and the contents, after acidulation with sulphuric acid, are distilled, an oily liquid passes over between  $78^\circ$  and  $208^\circ$ , consisting of methyl-propyl ketone (ethyl-acetone)  $C^2H^{10}O$ , together with a little alcohol, and afterwards between  $200^\circ$  and  $215^\circ$ , the ethylic ether of diethyl-di-acetic acid,  $C^2H^{10}O^2$ . The residue from the first distillation contains the soluble amide of ethyldiacetic acid  $C^2H^{10}NO^2$ . The insoluble amide is therefore resolved into the soluble amide and alcohol:

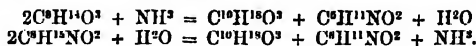


and the soluble amide is further resolved into methyl-propyl ketone, carbon dioxide, and ammonia:



Ethylic diethyl-di-acetate  $C^2H^{10}O^2$  is more easily obtained by heating ethylic ethyl-di-acetate with four or five times its volume of strong aqueous ammonia for several days to  $120^\circ$ – $130^\circ$ . The resulting oil, after being carefully dried, yields by fractional distillation, methyl-propyl ketone boiling at about  $100^\circ$ , unaltered ethylic ethyl-di-acetate boiling between  $190^\circ$  and  $200^\circ$ , and ethylic diethyl-di-acetate boiling between  $200^\circ$  and  $215^\circ$ .

From these results it would appear that in the decomposition of ethylic ethyl-di-acetate by ammonia at a high temperature, and also that of the insoluble ethylamide of ethyldiacetic acid by water, the soluble amide of ethyldiacetic acid is obtained together with a small quantity of ethylic ethyl-di-acetate, as represented by the following equations:



**ETHYLENE.** *Oxidation.*—According to F. Ludwig (*Ann. Ch. Pharm.* clxii. 47), ethylene heated with concentrated solution of *chromic acid* in sealed tubes is completely oxidised to carbonic acid and water; but at ordinary temperatures, intermediate products, viz. formic acid and perhaps also acetic acid, are likewise produced. Berthelot, on the other hand, found that ethylene, heated with concentrated chromic acid, in sealed tubes, was oxidised to aldehyde (*1st Suppl.* 602).

Ethylene is not taken up by *sulphuric acid* at ordinary temperatures, but at  $100^\circ$ , and, still better, between  $160^\circ$  and  $175^\circ$ , the gas is rapidly absorbed, and by subsequently diluting and distilling the acid liquid, a considerable quantity of alcohol may be produced. Elevation of temperature, then, being necessary to the absorption of ethylene by sulphuric acid, it appears not improbable that, in Berthelot's well-known experiment, the violent and continued shaking serves not only to bring the gas into intimate contact with the acid, but to develop the heat necessary.

Contact of ethylene with sulphuric acid at the temperatures above mentioned, does not give rise to condensation of the hydrocarbon. Neither does a still further elevation of temperature, or the employment of fuming sulphuric acid or of fluoride of boron produce signs of polymerisation. This remarkable stability in circumstances under which its higher homologues are easily affected, indicates that the constitution of ethylene is symmetrical, and not analogous to that of propylene, isobutylene, &c. (Gorjainow & Butlerow, *Ann. Ch. Pharm.* clxix. 196).



**Ethylene Bromide,  $C^2H^4Br^2$ .** Carius (*ibid.*) by heating this compound with water to  $150^{\circ}$ - $160^{\circ}$  obtained hydrobromic acid and aldehyde; Kriwaxin (*Zeitschr. f. Chem.* [2] vii. 263) obtained no aldehyde and only a doubtful trace of a condensed aldehyde.

**Decomposition by the Copper-zinc Couple.**—The dry couple has but little action on ethylene bromide, even at its boiling-point, the products being ethylene and zinc bromide. In presence of water, however, the bromide is easily decomposed at ordinary temperatures—zinc alone acts but slowly, the reaction in both cases being the same as with the dry couple :



In presence of alcohol, the couple acts with great violence, the products being still the same. With uncoated zinc-foil in presence of alcohol, no action takes place for half-an-hour, but it then proceeds rapidly and is terminated in about twenty minutes. The nature of the reaction being the same whether the couple is used in the dry state or moistened with water or alcohol, it appeared probable that the sluggishness of the action in the first case might be due to the insolubility of the zinc bromide in ethylene bromide. But when the ethylene bromide was diluted with twice its bulk of ether, the action was found to be much more sluggish than with water or alcohol: hence it appears that the nature of the solvent exerts some influence on the reaction (Gladstone & Tribe, *Chem. Soc. J.* [2], xii.)

**Bromethylene,  $C^2H^3Br$ .**—The reactions of this compound with haloid acids have been examined by Reiboul (*Ann. Ch. Pharm.* clv. 29, 212). When aqueous hydrobromic acid saturated at  $+6^{\circ}$  acts upon monobromethylene boiling at  $+18^{\circ}$  (3 to  $\frac{1}{2}$  vols. of the former to 1 vol. of the latter), ethylene bromide,  $C^2H^4Br^2$ , is formed slowly in the cold, more quickly at  $100^{\circ}$ ; but if the acid be diluted with  $\frac{1}{2}$  vol. water (its density then being  $55^{\circ}$  Bm.), combination takes place but slowly even at  $100^{\circ}$ ; and the product is not ethylene bromide, but bromethylene hydrobromide  $C^2H^3Br.HBr$ , identical with the bromethyl bromide formed by the action of bromine on ethyl bromide (*1st Suppl.* 594).

Hydrobromic acid saturated at  $+6^{\circ}$  does not act on this latter compound even at  $100^{\circ}$ .

Hydriodic acid acts on bromethylene in the same way as hydrobromic acid, excepting that the formation of isomeric compounds by it is determined, not by difference of concentration, but by difference of temperature.

Hydriodic acid saturated at  $+4^{\circ}$  combines somewhat rapidly with monobromethylene, the transformation being nearly complete in 6 or 7 days: the product consists of monobromethylene hydriodide  $C^2H^3Br.HI$ , which boils at  $141^{\circ}$ - $142^{\circ}$  under a pressure of 736 mm. and has a specific gravity of 2.5 at  $1^{\circ}$ . When treated with alcoholic potash or sodium ethylate, it gives up hydriodic acid and yields bromethylene. When hydriodic acid acts on bromethylene at  $100^{\circ}$  combination takes place quickly, the products being the hydriodide just mentioned, and the isomeric compounds ethylene iodobromide  $C^2H^4BrI$ , which may be separated by fractional distillation. Ethylene iodobromide boils, with partial decomposition, at  $160^{\circ}$  and has a specific gravity of 2.70 at  $1^{\circ}$ . If the hydriodic acid be diluted with  $\frac{1}{2}$  vol. water, it acts at  $100^{\circ}$  in the same manner though more slowly.

Hydrochloric acid saturated at  $0^{\circ}$ , does not appear to act on monobromethylene in the cold, but at  $100^{\circ}$  reaction takes place, and whether acid of  $26.5^{\circ}$  or of  $22^{\circ}$  Bm. be used, the product is the same, namely monobromethylene hydrochloride  $C^2H^3Br.HCl$ . This compound boils at  $81^{\circ}$ - $82^{\circ}$  and has a specific gravity of 1.61 at  $14^{\circ}$ . Alcoholic potash or sodium ethylate withdraws the hydrochloric acid, leaving monobromethylene.

Sodium methylate acts on bromethylene (also on iodethylene) at ordinary temperatures, even when shaded from sunlight; the products are the same as when the action takes place at a higher temperature, being acetylene, sodium bromide, methyl alcohol, and a trace of a substance which may be allyl alcohol, as it gives rise to an odour exactly resembling that of acrolein when treated with dilute sulphuric acid and potassium dichromate.

Pure potassium cyanide (prepared by saturating alcoholic potash with gaseous hydrocyanic acid) and silver cyanide have practically no action on bromethylene, even after several hours' heating at  $140^{\circ}$ - $150^{\circ}$ .

When bromethylene is kept in a sealed tube in the dark, no change ensues, even after several weeks; but if exposed to direct sunlight, it becomes changed into an isomeric, solid, non-crystalline, porcelain-like, elastic substance; this change takes place more rapidly with moist bromide than with the perfectly dry substance; the

presence of a small quantity of alcohol neither accelerates nor retards the change. This solid substance has the sp. gr. 2.705, whereas the liquid bromide has the sp. gr. 1.52 (Regnault). It begins to decompose at  $125^{\circ}$ – $130^{\circ}$ , and is but little acted on by boiling alcoholic potash; twelve hours heating to  $180^{\circ}$ – $200^{\circ}$ , with this reagent, however, forms a brown-black substance, insoluble in all menstrua, all bromine being removed from it without any evolution of gas. Sulphuric acid carbonises the substance on being heated with it; boiling nitric acid has but little action on it; bromine dissolves it, forming a loose compound, which splits up into bromine and the original substance on treatment with water, alcohol, or alkalis (E. Baumann, *Ann. Ch. Pharm.* clxiii. 308).

**Dibromethylene**  $C^2H^2Br^2$ .—In the preparation of this compound by digesting bromethylene bromide,  $C^2H^2Br.Br^2$ , with alcoholic potash (ii. 570) the formation of acetylene and bromoacetylene may be completely prevented by keeping the liquid cool, adding the potash to the bromide by drops, and not using more of it than is necessary to keep the mixture permanently alkaline. The resulting dibromethylene is separated by water, and then distilled on the water-bath, whereupon it distils almost wholly at  $75^{\circ}$ . Dibromethylene heated with alcoholic potash in an open vessel yields large quantities of bromoacetylene,  $C^2HBr$ ; but when it is heated with a large excess of alcoholic potash in a digestion tube, the product consists only of acetylene (Fontaine, *Compt. rend.* lxx. 1361).

**Ethylene Chloride**,  $C^2H^4Cl^2$ , is not attacked by common sulphuric acid, either at ordinary temperatures or at  $100^{\circ}$ , but at  $130^{\circ}$  complete decomposition takes place attended with separation of carbon (Oppenheim, *Deut. Chem. Ges. Ber.* ii. 441).

*Ethylene Chloride* is obtained in large quantity, together with some of its chlorinated derivatives, from the by-products of the manufacture of chloral. At Schering's factory in Berlin these by-products are collected by causing the vapours which issue from the alcohol retort, together with hydrochloric acid and excess of chlorine, to pass first through water, then through a series of condensers. The crude liquid thus obtained has been examined by Krämer (*Deut. Chem. Ges. Ber.* iii. 257). After a preliminary distillation to separate the ethyl chloride present, the residue (about 5 kilos) was submitted to fractional distillation, and the separate fractions were examined, either by further fractionation, or by first treating them with alcoholic potash (which acts especially, with separation of potassium chloride, on the higher boiling portions), and again separating them by distillation. In this manner the following compounds were isolated:—

1. *Ethylidene Chloride*,  $CH^3.CHCl^2$ , was obtained in pounds, as a liquid boiling at  $60^{\circ}$  (according to Regnault it boils at  $64^{\circ}$ ) not decomposed by cold alcoholic potash. Vapour-density, obs. = 49.54; calc. 49.5.

2. *Ethylene-chloride*,  $CH^2Cl.CH^2Cl$ , was obtained in considerable quantity. Boiling point  $85^{\circ}$ , vapour-density, obs. = 49.9, and 50.3.

3. *Monochlorethylene Chloride*,  $C^2H^3Cl.Cl^2$ , boiling at  $115^{\circ}$ . Vapour-density 66.6 and 68.1 (calc. 66.75). Easily resolved by alcoholic potash in the cold into potassium chloride and the following compounds:

4. *Dichlorethylene*,  $C^2H^2Cl^2$ .—This compound after purification boiled at  $35^{\circ}$  (Regnault gives  $35^{\circ}$ – $40^{\circ}$ ) and exhibited the characteristic property of changing, after a while, into a solid polymeric modification. On account of this transformation, the vapour-density came out somewhat higher than the calculated value: 49.35 instead of 48.5.

Regnault's chlorinated ethyl chloride,  $C^2H^3Cl^2$ , and the final product  $C^2Cl^4$ , were not found in the liquid examined by Krämer.

Monochlorethylene is changed by the action of sunshine into an isomeride similar in appearance and properties to the solid modification of bromethylene. Its sp. gr. is 1.406. It bears a heat of  $130^{\circ}$  without decomposition, but melts to a brown black mass at a higher temperature. It is not dissolved by bromine. Dichlorethylene is also changed by light into a solid isomeride which has been described by Regnault.

**Ethylene Cyanide**,  $C^2H^2.C^2N^2$ , or  $CH^3CN.CH^3CN$ , appears to be formed in the electrolysis of cyanacetic acid (p. 10).

**Ethylene Iodide**,  $C^2H^4I^2$ . When this compound is heated to  $85^{\circ}$ – $95^{\circ}$  in sealed tubes for 5 or 6 hours with acetylides of copper suspended in ether, and the ether is evaporated, an iodised compound is obtained, crystallising in broad concentrically grouped prisms and, after recrystallisation from alcohol, in pale yellow glistening prisms. It has an intensely allineous odour, quite different from that of acetylene, is not acted on by a mixture of strong nitric and sulphuric acids in the cold, but dissolves in hot sulphuric acid, forming a colourless liquid. Its composition has not yet been determined (Carstanjen u. Schortel, *J. pr. Chem.* [2], iv. 47).

*Iodethylene*,  $C^2H^2I$ , is formed, though only in small quantity, by the action of alcoholic potash on ethylene iodide; it is not produced by that of potassium iodide on bromoethylene. Sunlight decomposes it, liberating iodine, which probably prevents the isomeric transformation of the unaltered iodethylene (Baumann).

*Iodoethylenes*,  $C^2H^2I^2$ . Reboni, by treating bromoethylene with hydriodic acid, obtained two products having this composition, one boiling at  $142^\circ$ , the other at  $162^\circ$ ; and Lagermark (*Deut. Chem. Ges. Ber.* vi. 1211), by passing ethylene through a mixture of bromine and iodine in equivalent proportions, has obtained a third isomeric melting at  $25^\circ$  and boiling, with partial decomposition, at  $150^\circ$ . Mixed with an alcoholic solution of sodium acetate it yields iodethyl acetate,  $\begin{matrix} C^2H^2I \\ C^2H^2O \end{matrix}$ . A fourth isomeride appears to be produced by the action of hydrobromic acid on iodethylene.

**Sulphethers of Ethylene** (Bwerlöf, *Deut. Chem. Ges. Ber.* iv. 716). The following bodies have been obtained by the action of ethylene bromide on sodium mercaptide:—

*Ethylene-sulphonethyl*,  $C^2H^4 \begin{Bmatrix} SCH^3 \\ SCH^3 \end{Bmatrix}$ , boiling at  $185^\circ$ ; probably converted by fuming nitric acid into methylethylene-sulphin nitrate.

*Ethylene-sulphethyl*,  $C^2H^4 \begin{Bmatrix} SC^2H^3 \\ SC^2H^3 \end{Bmatrix}$ , boiling at  $210^\circ$ – $213^\circ$ ; oxidised by nitric acid to  $C^2H^4 \begin{Bmatrix} SOC^2H^3 \\ SOC^2H^3 \end{Bmatrix}$ , which forms glistening, crystalline scales, melting at  $170^\circ$ .

*Ethylene-sulphamyl*,  $C^2H^4 \begin{Bmatrix} SC^2H^3 \\ SC^2H^3 \end{Bmatrix}$ , boiling at  $245^\circ$ – $255^\circ$ , formed in like manner, is converted by oxidation into  $C^2H^4 \begin{Bmatrix} SOC^2H^3 \\ SOC^2H^3 \end{Bmatrix}$ , which is obtained in thin plates melting at  $45^\circ$ – $150^\circ$ .

*Ethylene-sulphophenyl*,  $C^2H^4 \begin{Bmatrix} SC^6H^5 \\ SC^6H^5 \end{Bmatrix}$ , white needles, insoluble in water, melting at  $65^\circ$ . By oxidation with chromic acid, it yields the compound  $C^2H^4 \begin{Bmatrix} SOC^6H^5 \\ SOC^6H^5 \end{Bmatrix}$ .

By the action of bromine the compound  $C^2H^4 \begin{Bmatrix} SBr^2C^2H^3 \\ SBr^2C^2H^3 \end{Bmatrix}$  is probably formed.

**ETHYLENE BASES.** The by-products of the manufacture of chloral contain, as already observed, large quantities of the dichlorides of ethylene and ethylidene. Now the latter compound is not attacked by alcoholic ammonia under  $160^\circ$ , and consequently the mixture of the higher boiling chlorides furnishes an excellent material for the preparation of the ethylene bases. On heating the fraction boiling between  $70^\circ$  and  $100^\circ$  for eight or ten hours to  $110^\circ$  with excess of alcoholic ammonia, the ethylene chloride is decomposed; and on filtering to remove sal-ammoniac, distilling and crystallising the residue from water, a large quantity of ethylene-diamine hydrochloride is obtained, crystallising in large shining needles. The mother-liquors, distilled with caustic soda, first yield ethylene-diamine, and the latter fractions contain the higher diamines and triamines (Hofmann, *Deut. Chem. Ges. Ber.* iv. 666).

*Ethylene-diamine Sulphate* crystallises in the quadratic system, but nevertheless exhibits the property of circular polarisation, a property not hitherto observed in any other body belonging to that system, except sulphate of strychnine. The circular polarisation of the ethylene-diamine salt is about three-fourths that of quartz. The crystals examined were partly dextro, partly levogyrate, but no hemihedral or hemisymmetric forms were observed in them (V. v. Lang, *Chem. Centr.* 1872, 178).

*Ethylene-diamine Sulphocyanate*.—Ethylene-diamine hydrochloride and silver sulphocyanate have no action on one another, but ethylene-diamine sulphocyanate can be readily prepared by saturating ethylene-diamine with sulphocyanic acid. It crystallises in large transparent prisms, which soon become opaque. It is insoluble in ether, very soluble in alcohol, and still more so in water. Even below its melting point, which is about  $145^\circ$ , it splits up into ammonium sulphocyanate and ethylene sulphocarbamide, no sulphocarbimide being formed. This decomposition is quite analogous to that which aniline sulphocyanate undergoes when heated (Hofmann, *Ann. Ch. Pharm.* lxx. 143).

*Tetraethylene-triamine*.—A mixture of ethylene bromide and alcoholic ammonia left to itself for several months, deposits considerable quantities of a white substance containing, together with ammonium bromide, an amorphous substance nearly insoluble in water, alcohol, and ether. This body appears, from analysis of the products of several preparations, to consist of the hydrobromides of one and the same ethylene base, probably belonging to the highest order of polyamines. The simplest atomic

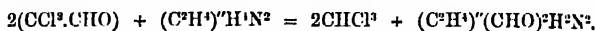
relations may be expressed by the formulæ  $(C^2H^4)^2HN^2.HBr$ ,  $(C^2H^4)^2HN^2.2HBr$ , and  $(C^2H^4)^2HN^2.3HBr$ , which represent the hydrobromides of tetraethylene-triamine. By prolonged boiling with ammonia the hydrobromic acid is removed and the corresponding hydrides, resembling the hydrobromides in being amorphous and uncrySTALLISABLE, were produced (Hofmann, *Deut. Chem. Ges. Ber.* iii. 141).

**ETHYLENE DIAMIDES.** A mixture of benzoyl chloride and ethylene-diamine, after it has become cool, solidifies to a crystalline mixture of ethylene-diamine

hydrochloride and ethylene-dibenzoyl-diamide,  $C^{10}H^{16}N^2O^2 = \left( \begin{smallmatrix} (C^2H^4)^2 \\ (C^2H^4)^2 \\ H^2 \end{smallmatrix} \right) N^2$ ,

which crystallises in needles slightly soluble in alcohol, but insoluble in water.

Ethylene-diformyl-diamide,  $\left( \begin{smallmatrix} (C^2H^4)^2 \\ (CHO)^2 \\ H^2 \end{smallmatrix} \right) N^2$ , is formed, with elimination of chloroform, by the action of chloral on ethylene-diamine:



It is a transparent syrup, easily decomposed into ethylene-diamine and formic acid by the action of alkalis or acids. In a similar manner ethyl-formamido, boiling at  $199^\circ$ , may be obtained from chlorine and ethylamine.

A mixture of ethyl oxalate and a strong alcoholic solution of ethylene-diamine becomes almost solid, from deposition of ethylene-oxamide,  $(C^2H^4)^2(C^2O^2)^2H^2N^2$ , an amorphous substance nearly insoluble in alcohol and in water. The mother-liquors yield, on evaporation, ethylic ethylene-oxamate,  $C^{10}H^{16}N^2O^6 = \left( \begin{smallmatrix} (C^2H^4)^2(C^2O^2)^2H^2N^2 \\ (C^2H^3)^2 \end{smallmatrix} \right) O^2$ , which crystallises in white scales very soluble in alcohol and water (Hofmann, *Deut. Chem. Ges. Ber.* v. 240).

**ETHYLENE-GLYCOL DINITRIN.** See NITRINS.

**ETHYLENE-IRIDIUM COMPOUNDS.** See IRIDIUM.

**ETHYLENE-IRON BROMIDE.** See IRON.

**ETHYLENE-PLATINUM COMPOUNDS.** See PLATINUM.

**ETHYLENE-PROTocatechuic Acid.** See PROTocatechuic Acid.

**ETHYLENE-SULPHOCARBAMIDE or ETHYLENE-SULPHURIA,**

$C^2H^4N^2S = \left( \begin{smallmatrix} (C^2H^4)^2 \\ (CS)^2 \\ H^2 \end{smallmatrix} \right) N^2$ . An alcoholic solution of ethylene-diamine mixed with

carbon bisulphide deposits in a short time a white and nearly amorphous compound, having the composition  $C^2H^4N^2S^2 = (C^2H^4)^2H^2N^2.CS^2$ . This compound is almost insoluble in alcohol and ether, but dissolves in warm water with partial decomposition, and, provided the solution has not been boiled, is again deposited, on cooling, in prismatic crystals. It does not yield ethylene-diamine when treated with alkalis, and is therefore not the ethylene-sulphocarbonate of ethylene-diamine. On boiling it with water, hydrogen sulphide is given off, and ethylene-sulphocarbamide is formed:  $C^2H^4N^2S^2 = C^2H^4N^2S + H^2S$ . This amide is soluble in water, and separates from its aqueous solution in prismatic crystals having an extremely bitter taste. It is only slightly soluble in ether, but dissolves readily in alcohol. It melts at  $194^\circ$ , and is decomposed at a higher temperature. It is also formed by the action of dilute acids on solutions of metallic salts. A mercury-compound,  $2(C^2H^4)^2N^2S.3HgCl^2$ , and a bright yellow amorphous platinum-compound,  $2(C^2H^4)^2N^2S.PtCl^4$ , have been prepared. On heating the urea with strong sulphuric acid, diluting with water, and adding platinum-chloride, a second salt is obtained, crystallising in long needles,  $2(C^2H^4)^2N^2S.HCl.PtCl^4$ . When, however, this salt is decomposed by sulphuretted hydrogen and platinum chloride is added to the hydrochloric acid solution, the original amorphous platinum compound is precipitated. Ethylene-sulphocarbamide, which is intermediate between ethylene-diamine and ethylene-disulphocarbamide,



is very stable, not being altered by long digestion at a high temperature with carbon disulphide or with carbon disulphide and lead oxide (Hofmann, *Deut. Chem. Ges. Ber.* v. 240).

**ETHYL-GLYCID**,  $C^2H^4O^2 = C^2H^3 \begin{Bmatrix} OC^2H^3 \\ O \end{Bmatrix}$ , is produced by distilling monox-ethyl-chlorhydrin,  $C^2H^3Cl(OH)(OC^2H^3)$ , the product of the action of cold dilute hypochlorous acid on allyl-ethyl oxide (p. 49) with caustic potash. It is a colourless mobile liquid having an agreeable odour and very pungent taste; soluble in water, and combining readily with the haloid acids. Phosphorus pentachloride converts it into  $C^2H^3(OC^2H^3)Cl^2$ , a body which is also produced by the action of chlorine on allyl-ethyl oxide (L. Henry, *Deut. Chem. Ges. Ber.* v. 449).

**ETHYLIDENE COMPOUNDS.** *Bromide*,  $CH^3.CHBr^2$ .—Chlorinated ethyl chloride is known to be identical with ethylidene chloride (1st Suppl. 606), whereas brominated ethyl bromide differs entirely from the so-called ethylidene bromide which Wurtz and Frapolli (*Ann. Ch. Phys.* lvi. 144) obtained by the action of phosphorus pentabromide on aldehyde. Hence there has existed considerable doubt whether the latter compound is really the bromide of ethylidene. This question has lately been examined by Paternò n. Pisati (*Gazzetta chimica italiana*, i. 596). By treating dichloraldehyde with phosphorus pentachloride, they have obtained results which seem to show that the product of the action of phosphorus pentabromide on aldehyde is an oxybromide of ethylidene analogous to the oxychloride described by Lieben. On adding aldehyde to *phosphorus bromochloride*,  $PCl^3Br^2$ , treating the product with water, and distilling in a current of steam, an oily product is obtained which, by rectification, gives a liquid of the formula  $C^2H^3Br^2$ , boiling at  $110^\circ$ – $112^\circ$ . Its mode of formation shows it to be the true ethylidene bromide, and from its boiling point it would seem to be identical with the brominated ethyl bromide obtained by Hofmann and Caventon by the action of bromine on ethyl bromide, and by Reboul (*Compt. rend.* lxx. 399) by that of hydrogen bromide on brominated ethylene. The less volatile portion of the product appears to contain more highly brominated derivatives of ethylidene, an analysis of the portion boiling at about  $180^\circ$  corresponding very nearly with the formula  $C^2H^3Br^2$ .

*Ethylidene Chloride*,  $CH^3-CHCl^2$ , is obtained in considerable quantity from the by-products of the manufacture of chloral (p. 490).

*Trichlorethylidene Glycol*,  $CCl^3-CH \begin{Bmatrix} OH \\ OH \end{Bmatrix}$  is identical with chloral hydrate, and its ethylic ether,  $CCl^3-CH \begin{Bmatrix} OH \\ OC^2H^3 \end{Bmatrix}$ , with chloral alcoholate (p. 314).

**ETHYL-METHYL CARBINOL**,  $(C^2H^3)(CH^3).CHOH$ . See BUTYL ALCOHOLS (p. 218).

**ETHYLOXY-OXALYL CHLORIDE**,  $COCl-CO(OC^2H^3)$ . See OXALIC ETHERS.

**ETHYL-PHOSPHINES** }  
**ETHYL-PHOSPHINIC ACID** } . See PHOSPHINES.

**ETHYL-PHOSPHOPLATINOUS COMPOUNDS**. See PHOSPHOPLATINUM COMPOUNDS.

**ETHYL-THIOSULPHURIC ACID**,  $C^2H^3S^2O^2 = C^2H^3 \begin{Bmatrix} S^2O^2 \\ H \end{Bmatrix}$ . *Ethyl-hypo-sulphurous acid*.—This acid is produced by treating ethyl sulphide (boiling at  $81^\circ$ ) with an equal volume of strong sulphuric acid. On adding water, saturating with barium carbonate, and concentrating, the liquid deposits colourless rectangular tables with truncated summits, having the composition  $C^2H^3BaS^2O^2$  or  $(C^2H^3S^2O^2)Ba + 2H^2O$ ; this salt is easily soluble in water, less soluble in alcohol. The copper salt prepared from it forms small quadratic tables very soluble in water. The silver salt crystallises in small shining laminae. The hydrogen salt or free acid does not appear to have been obtained (R. H. Smith, *Chem. Soc. J.* [2], vii. 302).

**EUCALYPTOL**,  $C^{10}H^{18}O$  (Clocz, *Ann. Ch. Pharm.* cliv. 372).—This compound is contained in large quantity in the volatile oil of *Eucalyptus globulus*, a tree indigenous in Tasmania, and much cultivated in the south-west of Europe. The crude oil contains also a number of products boiling between  $188^\circ$  and  $190^\circ$ , and above  $200^\circ$ , the eucalyptol being contained in the portion which passes over between  $170^\circ$  and  $178^\circ$ , from which it may be obtained pure by contact, first with solid potassium hydrate, then with calcium chloride, and subsequent distillation.

Eucalyptol boils at  $175^\circ$ , has a specific gravity of 0.905 at  $8^\circ$ , and turns the plane of polarisation to the right. Its molecular rotatory power is  $+10.42^\circ$  for a length of 100 mm. It is slightly soluble in water and dissolves completely in alcohol; the dilute solution has an odour of roses. Vapour-density, obs. = 5.92, calc. = 6.22.

Ordinary nitric acid slowly attacks eucalyptol, forming, amongst other products, an acid probably analogous to camphoric acid. Strong sulphuric acid blackens eucalyptol,

and water separates from the product a tarry body which yields by distillation a volatile hydrocarbon.

Eucalyptol heated with phosphoric anhydride gives up water, and yields eucalyptone,  $C^{12}H^{18}$  (vapour-density = 5.3) which boils at  $165^{\circ}$ , and has a specific gravity of 0.836 at  $12^{\circ}$ . At the same time there is formed another liquid, eucalyptolene, which has the same composition, but boils above  $300^{\circ}$ . Eucalyptol absorbs a large quantity of dry hydrogen chloride, the liquid first solidifying to a crystalline mass, which, however, afterwards liquefies, with separation of water, and formation of a body apparently identical with eucalyptone.

**EUDIALYTE and EUKOLITE.**—From the analysis of eudialyte from Greenland (A), and of eukolite from the zircon-syenite of Norway (B), Nylander (*Jahrb. f. Mineralogie*, 1870, 488) concludes that both these minerals are included in the formula,  $RO.2(SiO_2.ZrO_2)$  given by Rammeisberg for the former.

	SiO <sup>a</sup>	ZrO <sup>a</sup>	CaO	FeO	MnO	CaO	Na <sup>o</sup> O	Cl	X†
A. 51.86	14.67	-	6.5†	1.46	9.82	12.32	1.37	1.43	= 99.47
B. 50.47	14.26*	4.30	5.42	3.67	9.58	10.46	1.68	1.57	= 101.41

\* Loss by ignition.

† Together with Ta<sup>o</sup>O<sub>2</sub>.

**EUGENOL or EUGENIC ACID**,  $C^{10}H^{10}O^2$ . The formula  $C^6H^7 \left\{ \begin{array}{l} OH \\ OCH^3, \text{ as} \\ C^4H^3 \end{array} \right.$

assigned to this body on account of the formation of methyl iodide by heating it with hydriodic acid, and of protocatechuic acid,  $C^6H^7(OH)^2$ . COOH, by fusing it with potash, (1st Suppl. 609), is further supported by the fact recently observed by Grube and Borgmann (*Ann. Ch. Pharm.* clviii. 282), that methyl eugenate,  $C^6H^7(OCH^3)^2C^4H^3$ , when oxidised by chromic acid, is converted into dimethoxybenzoic acid  $C^6H^7(OCH^3)^2CO^2H$ . The methylic ether, obtained by heating sodium eugenate with methyl iodide, was dissolved in glacial acetic acid and heated for two or three days on a water-bath with 2 parts of powdered potassium dichromate; the liquid was then diluted with water, and either added to separate any unchanged methyl eugenate; the ethereal solution was shaken with a solution of ammonium carbonate; and the alkaline liquid concentrated. On addition of an acid, a crystalline substance separated, which, after recrystallisation from hot water, exhibited the composition of dimethoxybenzoic acid.

*Ethyl eugenate* (which boils at  $251^{\circ}$  and not at  $240^{\circ}$ , as stated by Cahours) is converted by oxidation into the corresponding diethoxybenzoic acid. Eugenol itself gives by direct oxidation merely a brownish non-crystalline mass, not soluble in water, alcohol, benzene, or any other solvent, and not yielding any definite chemical compound. When heated, it gave off carbonic anhydride and water, while the residue smouldered away on exposure to the air, leaving pure chromic oxide.

**EUKOLITE.** See EUDIALYTE.

**EULYTE and DYSLYTE.** These names were given by Baup to two substances which he obtained by the action of strong nitric acid on citraconic acid, the more soluble being called *eulyte*, the less soluble, *dyslyte* (ii. 606). They have lately been more fully examined by Bassett (*Chem. Soc. J.* [2], x. 98).

To prepare them, crystallised citraconic acid was treated with nitric acid of sp. gr. 1.45, using 10 grams of the former to 15 grams of the latter—larger quantities being found to cause a too violent reaction. The mixture was gently heated until action commenced, and the lamp then removed. After completion of the reaction, when most of the nitric acid was decomposed or driven off, the solution deposited an oil, the quantity of which was increased by adding a certain quantity of water. The oil was then washed two or three times with fresh quantities of water. It remains fluid occasionally for days, unless touched with a glass rod, when it crystallises in a short time. The acid mother-liquor contains a large quantity of oxalic, and some mesoconic acid.

The oily product, the quantity of which is very small, consists of a mixture of two neutral crystalline substances, and a small quantity of a yellow oil. The complete separation of these is a matter of considerable difficulty, notwithstanding their great difference in solubility in alcohol, from the fact that the less soluble substance is easily taken up and obstinately held in solution in presence of the more soluble body, which is the main product of the reaction. They may, however, be obtained pure by numerous fractional recrystallisations.

*Eulyte*,  $C^6H^8N^1O^1$ , the more soluble substance, agrees perfectly in character with the eulyte of Baup. It is best crystallised from warm chloroform, which deposits it on cooling in large crystals belonging to the quadrate system, with very perfect and brilliant faces. It melts at  $99.5^{\circ}$  (corr.), but its solidifying point is very uncertain, as

it occasionally remains fluid for hours unless touched with a hard body. By very careful heating, it appears to sublime unchanged, but decomposes at a high temperature with evolution of nitrous fumes, and if in somewhat large quantity, with violent combustion.

Eulyte gives by analysis (mean), 29.26 p.c. carbon, 2.61 hydrogen and 22.60 nitrogen, the formula requiring 29.27 C., 2.52 H., and 22.76 N. Heated with alcoholic potash, it is decomposed, with formation of a nitrite, and a brown resin soluble in alkalis. When moderately heated with tin and hydrochloric acid, it yields ammonia, and a volatile base smelling like picoline. In one experiment a solid base was also obtained, precipitated by ammonia, soluble in potash, and forming an oily hydrochloride almost insoluble in cold water, but soluble in alcohol.

*Dyslyte*,  $C^{10}H^8N^4O^8$ , separates from boiling alcohol, in which it is sparingly soluble, in long needles melting at  $189^\circ$  (corr.) On cooling it solidifies suddenly, but at temperatures varying between  $135^\circ$  and  $165^\circ$ . It gives by analysis 37.80 p.c. carbon, 2.50 hydrogen and 21.97 nitrogen, the formula requiring 37.80 C., 2.36 H., and 22.05 N. It is decomposed by alcoholic potash, with formation of brown resinous products.

The fluid product accompanying the two solid substances was precipitated by water from the last mother-liquors of the crude product, and purified as far as possible by distillation in a current of steam (a small quantity of the solid products coming over also), and the distillate shaken up with ether. On evaporation of the clear ethereal solution, a small quantity of a yellow oil remained, having the characteristic smell of volatile nitro-compounds. On the application of a strong heat, it exploded violently. On reduction it gave apparently but ammonia, and some tarry matter.

**EUPHORBIA.** The flowers of *Euphorbia Cyparissias* yield a yellow colouring matter called luteic acid, which has been prepared and examined by H. Höhn (*Arch. Pharm.* [2] xli. 218). The fresh flowers are exhausted with alcohol of 60 p.c., the greater part of the alcohol distilled off, and the residual liquid filtered and precipitated with basic lead acetate. The well-washed precipitate is suspended in warm water, decomposed by hydrogen sulphide, and the filtrate is evaporated and left to stand over sulphuric acid. Yellowish green crusts then separate, an additional quantity of which may be obtained by evaporating the mother-liquor, dissolving the residue in alcohol, precipitating with ether, and evaporating the filtered solution. A further quantity of the same product may also be obtained in greenish-yellow crusts or warty aggregations by exhausting the precipitated lead sulphide with hot alcohol, and distilling. The colouring matter thus produced may be purified by washing it thoroughly with cold water, then digesting with a little ether, to remove a green soft resin and chlorophyll, dissolving in ether-alcohol, leaving the solution to evaporate slowly, and recrystallising the residue, which is then tolerably pure, several times from hot water mixed with 3 or 4 p.c. of alcohol; five kilos. of fresh flowers yield about 3 grams of pure substance.

The colouring matter is pure yellow, and crystallises in slender needles which appear under the microscope as four-sided, or more rarely as six-sided prisms with perpendicular or less frequently with oblique end-faces. It sometimes separates from a hot aqueous solution in granular, amorphous, or spherical warty groups. It is scentless; has a bitterish, somewhat astringent taste; sublimates at about  $220^\circ$  in yellow flocks made up of shining needles; melts at  $273^\circ$ – $274^\circ$ ; dissolves in 11,000 parts of cold, and 3,400 parts of boiling water, in 28.7 parts of cold absolute alcohol, and in 27.2 parts of ether. The solutions have an acid reaction, and the body exhibits generally the characters of an acid. The name *luteic acid* has been given to it by Höhn, because it exhibits considerable resemblance to luteolin, and, like the latter, yields protocatechuic acid when fused with potash. It dissolves in caustic and carbonated alkalis with a dark yellow to reddish-yellow colour, the solutions yielding green or yellow-brown precipitates with metallic salts. It reduces silver nitrate, mercurous nitrate, and alkaline cupric solutions, when heated therewith. With ferric chloride, it forms a solution having a fine green colour, changing after a while to red-brown on further addition of the iron solution. Strong sulphuric acid dissolves the colouring matter with yellow colour, and water separates it again in yellow flocks. It is not altered by boiling with dilute sulphuric acid, and is, therefore, not a glucoside. It dissolves easily in acetic and in strong nitric acid, and is oxidised to oxalic acid by boiling with the latter. By distillation with potassium chromate and dilute sulphuric acid, it yields an acid distillate which reduces silver solution and therefore probably contains formic acid. By evaporation of the aqueous solution, the colour becomes continually darker, and a red residue is finally obtained, no longer soluble in water or in alcohol. Höhn assigns to this colouring matter the formula  $C^{10}H^{10}O^{10}$ , but the analyses from which it is deduced differ considerably from one another.

**EUXENITE.** The following analyses of this mineral have lately been published:

a. From Hitterö (John, *Pogg. Ann.* clxiv. 594); b. From Alvö near Arendal, sp. gr. 4.984–5 vol. (Rammelsberg, *Chem. Soc. J.* [2], x. 200); c. From the same (Forbes a. Dahll, *ibid.* 293); d. From Morefjär near Arendal, sp. gr. = 4.672 (Rammelsberg, *loc. cit.*); e. From Eydland, Lindernäs, sp. gr. = 5.058–5.103 (Rammelsberg, *loc. cit.*); f. From the same, sp. gr. 5.103 (Behrend, *Deut. Chem. Ges. Ber.* i. 224);

	a.	b.	c.	d.	e.	f.
Niobic oxide . . .	18.37	35.09	32.58	34.59	33.39	31.08
Titanic oxide . . .	34.96	21.16	14.36	23.49	20.03	19.17
Alumina . . .	5.41	—	3.12	—	—	—
Ceric oxide . . .	8.43	—	3.31	—	—	—
Corous oxide . . .	—	3.17	—	2.26	3.50	2.81
Yttria . . .	13.20	27.48	29.36	16.63	14.60	18.23
Erbia . . .	—	3.40	—	9.06	7.30	—
Uranous oxide . . .	7.75	4.78	5.22	8.55	12.12	19.52
Ferrous oxide . . .	2.54	1.38	1.98	3.19	3.25	4.77
Magnesia . . .	3.92	—	6.19	—	—	—
Lime . . .	1.63	—	1.37	—	1.36	1.19
Potash . . .	—	—	—	—	0.82	—
Water . . .	2.87	2.63	2.88	3.47	2.10	2.40
	99.08	99.09	100.37	101.51	98.77	100.10

The composition of the euxenite of Hitterö differs considerably from that of all the rest, especially in the predominance of the titanic over the niobic acid, and in the large proportion of the cerum oxide.

**EVERNIC ACID**,  $C^{12}H^{10}O^7$ . This acid is obtained, together with usnic acid, by macerating *Evernia prunastri* with milk of lime, and precipitating the filtered solution with hydrochloric acid: it is extracted from the dried precipitate by repeated treatment for a short time with boiling alcohol, precipitated by water, and recrystallised, without further digestion, from strong alcohol. It forms groups of small needles which melt at  $164^\circ$ ; does not decompose solutions of sodium bicarbonate in the cold; its calcium salt is decomposed by carbonic acid. When treated with potash or baryta, it yields, as formerly stated (ii. 611), only one fixed product, viz. overnicnic acid  $C^{12}H^{10}O^4$ .

*Tetrahromevernica acid*,  $C^{12}H^{12}Br^4O^7$ , is obtained by treating perfectly dry finely pulverised evernicacid with a slight excess of anhydrous bromine, washing with carbon sulphide, and repeated crystallisation from boiling alcohol, from which it separates, after long standing, in small colourless prisms. It is insoluble in water and in carbon sulphide, slightly soluble in hot benzene, easily in ether, melts at  $161^\circ$  (Stenhouse, *Proc. Roy. Soc.* xviii. 222).

**EXCREMENTS.** The excrements of the common bat, and of the Egyptian bat, have been examined by O. Popp (*Ann. Ch. Pharm.* clv. 351; clviii. 115). Those of the Egyptian bat are found in caves in stalactitic masses. They dissolve easily and almost completely in water and in alcohol, have an acid reaction, and yield by analysis 37.2 p.c. nitrogen. They contain 77.80 p.c. urea, 1.25 uric acid, 2.55 creatine, 13.45 sodium phosphate,  $Na^2HPO^4$ , 3.66 water given off at  $100^\circ$ , and 0.575 insoluble residue (= 99.285); they appear also to contain a little xanthine. From this composition it is evident that these excrements consist of the urine of the animal. It is not known what becomes of the faeces, or why the urine should be free from them. The non-decomposition of the urea is due to the dryness and warmth of the climate.

The excrement of the common bat (*Rhinolophus Hipposiderus*) was collected from a locality where it had accumulated to the thickness of three inches. It was in the form of dry, small, long, granular masses, of a dark brown colour, and was obviously composed of the faeces of the animal intermingled with the decomposition-products of the urine, viz., ammonia salts. It contained not a trace of urea, and no uric or oxalic acids. The chief portion seemed to be made up of the undigested wing-cases of insects. Cold solution of soda extracted a brown humus-like body, with abundant evolution of ammonia. Dried at  $100^\circ$  the excrement yielded 8.25 per cent. of nitrogen, and 6.25 per cent. of ash, containing potassium, sodium, calcium, magnesium, ferric oxide, chlorine, sulphuric, silicic, and 36 per cent. of phosphoric acid.

**EXCRETIN.** Marcet, who discovered this body, assigned to it the formula  $C^{12}H^{10}SO^4$  (ii. 614). But, according to Hinterberger (*Ann. Ch. Pharm.* clxvi. 213),



the body thus formulated is a mixture. Pure excretin contains no sulphur, and has the composition  $C^{20}H^{16}O$ . It is obtained by exhausting fresh excrements with boiling alcohol, and leaving the solution to stand for a week. A black precipitate then separates out, containing excretin and the salt  $C^{20}H^{13}MgNO^{11}$ . The filtrate is precipitated with milk of lime, and the dried precipitate treated with a hot mixture of ether and alcohol. On exposing the solution during a week to a temperature below  $0^{\circ}$ , crude excretin crystallises out in semi-globular masses consisting of yellow needles. It is purified by crystallising it repeatedly from alcohol, with addition of blood-charcoal, the temperature being kept below  $0^{\circ}$ . Bromine converts it into dibrom-excretin,  $(C^{20}H^{13}Br^2O)$ , which separates from a mixture of ether and alcohol in hard brittle crystals grouped in globular masses. A crystalline chlorine-compound could not be obtained. 100 pounds of fresh excrements yielded 8 grams of pure excretin.

**EXPLOSION.** The conditions which determine the explosive force of gun-powder and other detonating substances have been discussed by Berthelot (*Mém. Scientifique*, 1871, 40). He points out that, for the expression of explosive force, four data are necessary, viz. 1st. The composition of the substance. 2nd. The composition of the products of the explosion. 3rd. The quantity of heat disengaged in the reaction. 4th. The volume of gas produced.

The composition of the products of the explosion may be predicted in all cases when the substance contains sufficient oxygen to form stable, completely oxidised compounds. But if the quantity of oxygen is less than this, the nature of the products will vary with the pressure, temperature, work done, &c., and cannot be predicted: in the calculations under consideration, Berthelot adopts the simplest expressions consistent with known facts.

The quantity of heat disengaged may be experimentally determined, and if the reaction be accurately known, it may also be calculated. The maximum work that can be effected by any explosive material is proportional to the heat evolved.

The volume of gas produced may be experimentally determined, and may also be calculated, if the reaction be accurately known.

With these data the pressure produced might easily be calculated if Boyle's law held good under the conditions of the experiment, and if the specific heat of the gases remained constant; but this latter probably varies with the temperature and pressure, and is entirely unknown, whilst the laws of Boyle and Gay-Lussac are wholly inapplicable to gases under a pressure of several thousand atmospheres. As, however, it is necessary to use some comparative expression for the pressure produced by different explosive substances, the product of the volume of the gases (reduced) into the quantity of heat in units is employed for that purpose, not as being an exact measure of the true pressure, but as being obtained from two characteristic and experimental elements.

To gain a complete notion of the reactions occurring at the explosion, it is necessary to bear in mind the phenomena of dissociation, according to which, the products found after cooling do not exist at the high temperature produced by the explosion, but are replaced by more simple compounds. Hence it follows that the quantity of heat corresponding with the actual reactions is less than the quantity calculated from the products found after cooling.

Under the enormous pressure produced by the explosion, it is probable that the pressure varies much more rapidly with the temperature than is admitted by Boyle's law, and as the combinations of elements, other conditions being the same, advance in complexity with the pressure, as shown by Berthelot's experiments on the decomposition of acetylene at various pressures by the electric spark (*Ann. Ch. Phys.* [4], xviii. 196), it will be seen that considerable modifications of the phenomena of dissociation must ensue. This increased influence of pressure may, therefore, be supposed to compensate the decomposing influence of heat.

The phenomena of dissociation doubtless appear at the very commencement of the expansion of the gases; for as the gas expands, it cools, and its elements re-arrange themselves in more complicated compounds; this produces a fresh disengagement of heat, and this action continues during the whole time of expansion. The actual pressure will, therefore, always be higher than the pressure calculated from the quantity of heat disengaged at the moment of maximum temperature, and at first it will be lower than the pressure calculated from the results given by the calorimeter; but as the volume increases, this difference will diminish, and, finally, disappear, the reactions being gradually completed with constant disengagement of heat.

The total quantity of heat, and, consequently, the maximum work done by burning the substance in a known space may be calculated without regard to dissociation, if the final temperature and state of combination of the elements of the products are exactly known.

2nd Sup.

The following table exhibits the heat evolved in the combustion of various explosive compounds, the volume of gas produced, and the product of these two numbers:—

	Quantity of heat evolved by 1 kilo, in units	Volume of gas formed	Product of these two numbers, to serve as a term of comparison of the pressures produced
		cub. cent.	
Sporting powder . . . . .	644000	0·216	139000
Military powder . . . . .	622500	0·225	140000
Blasting powder . . . . .	380000	0·355	135000
Powder with excess of charcoal . . . . .	429000	0·510	219000
Powder made with sodium nitrate . . . . .	769000	0·252	194000
" " potassium chlorate . . . . .	972000	0·318	309000
Chloride of nitrogen . . . . .	316000	0·370	117000
Nitroglycerin . . . . .	1282000	0·710	910000
Gun-cotton . . . . .	700000	0·801	560000
" with nitre . . . . .	1018000	0·184	492000
" with potassium chlorate . . . . .	1446000	0·484	700000
Potassium picrate . . . . .	872000	0·585	510000
" with nitre . . . . .	957000	0·337	323000
Picrate with potassium chlorate . . . . .	1405000	0·337	474000

*Ordinary Gunpowder.*—On comparing the actual products of the explosion with the results of the theoretical equation,  $2\text{NO}^*\text{K} + \text{S} + 3\text{C} = 3\text{CO}^2 + \text{K}^2\text{S} + \text{N}^2$ , it appears that the quantity of heat developed in the theoretical reaction is much less than that actually produced: hence it may be inferred that those products are most readily produced, in the formation of which the greatest quantity of heat is evolved, the pressure, represented by 139,000, being the same.

*Powder containing sodium nitrate* was largely employed in excavating the Suez Canal, and with considerable economy: for experiment shows that the substitution of sodium for potassium in any definite salt occasions a nearly constant disengagement of heat. As the alkaline metal exists as a salt, both before and after the explosion, this influence is eliminated if the quantity of heat be calculated for equivalent weights of sodium and potassium salts; but, with equal weights, the volume of gas and the heat, consequently the total work done, will be greater in the case of sodium nitrate, the equivalent of sodium being lower than that of potassium.

*Powder containing potassium chlorate.*—The extreme rapidity with which this powder explodes is due to the enormous quantity of heat evolved by the explosion of the particles first ignited, to the low specific heat of the products, and the comparatively low temperatures at which the chlorate decomposes. As the products are the most simple and stable possible, being binary compounds, the progressive effects of dissociation are less marked, and the variations of pressure during the expansion of the gases are not affected by recombinations of the elements successively produced during cooling. Hence the great detonating quality of this powder. Similar remarks are applicable in a still higher degree to *chloride of nitrogen*.

*Nitroglycerin* combines the properties of chloride of nitrogen and ordinary gunpowder. This is explicable by considering the effects of dissociation. At the first moment the elements of water and carbon dioxide are separated; but as they recombine during expansion, fresh quantities of heat are evolved, and regulate the fall of the pressure; therefore during expansion nitroglycerin behaves as ordinary gunpowder; but the effects of dissociation are less evident, because the products are more simple, and the initial pressure is higher.

Bertholot also discusses, from the thermodynamic point of view the experiments described by Abel (*1st Suppl.* 486), on the detonation of nitroglycerin and gun-cotton. Taking the case of the explosion of nitroglycerin produced by a falling weight, Bertholot calculates that the impact of a weight of several kilos. falling through 0·5m. would raise the temperature of a mass of nitroglycerin but a fraction of a degree, if the heat were distributed equally throughout the mass; but the conversion of motion into heat is too sudden to allow of this distribution; the particles struck may therefore attain the exploding point,  $190^\circ$ ; a large quantity of gas is suddenly produced, and this produces a second and more violent shock on the adjacent particles before they have had time to escape, from the sphere of action. The force so developed is also

converted into heat, and in this way a continuous succession of changes is established throughout the whole mass. The violence of the initial decomposition will increase with the intensity of the first shock, and consequently the pressures produced throughout the entire series of decompositions will rise in equal proportion. Hence one and the same explosive substance will behave in different ways, according to the manner of its inflammation.

These effects are less marked in the case of loose gun-cotton, on account of the large quantity of air interspersed through its bulk. As compressed gun-cotton is less compact than nitroglycerin, it should follow that it is less easily detonated than nitroglycerin; and this is found to be the case. Nitroglycerin may be detonated by the fall of a weight from a moderate height, by a gun-cotton fuse, or by a mixture of potassium chlorate and fulminate of mercury. Gun-cotton detonates only with pure fulminate of mercury, and the best results are not obtained unless the fulminate be enclosed in a rather thick case of sheet-tin, and placed in contact with the gun-cotton, conditions which realise the greatest initial pressure. The quantity of force thus converted depends on the suddenness of the shock, and on the amount of work which it is capable of doing. These elements vary with the detonator, and Abel has found that chloride of nitrogen is not very efficacious, and that iodide of nitrogen, which explodes by the slightest friction, is incapable of exploding gun-cotton. But chloride of nitrogen develops less heat than any other compound here treated of (see table), therefore a larger quantity of it must be employed, and judging by analogies drawn from other iodine substitution-substances, iodide of nitrogen should develop less heat and work than the same weight of chloride of nitrogen: hence its inactivity in this respect.

Dynamite is found to possess less bursting or breaking power than nitroglycerin; this is explained by the intervention of the inert material, which shares with the nitroglycerin the heat developed by the exploding shock. Thus silica and alumina have nearly the same specific heat as the gaseous products of the explosion of nitroglycerin, the volume being constant; if therefore equal weights of nitroglycerin and either of these substances be fired in a space filled by the mixture, the silica or alumina will absorb half the heat, and proportionally reduce the pressure.

On comparing nitroglycerin with gunpowder, it will be seen that if a given weight of nitro were converted into the exactly equivalent weight of nitroglycerin, it would, in a blast, develop three times as great a pressure as would be produced by the gunpowder made with the same quantity of nitro.

Gun-cotton does not, like nitroglycerin, contain sufficient oxygen for its complete combustion; the products formed on explosion are therefore highly complex. It differs from other explosive substances rather by greater initial pressure than by maximum work; and the empirical results of Piobert [*Traité d'Artillerie, partie théorique*, 196] agree with the calculated result (see table). Theory shows the desirability of causing gun-cotton to explode in the smallest possible space, as practised by Abel in compressing it.

More work may be obtained from gun-cotton by adding to it nitro or potassium chlorate; but as the combustion is then complete, the effects of dissociation during expansion of the products are less evident, and the mixture acquires greater bursting power.

Potassium picrate does not contain sufficient oxygen for its perfect combustion, and is intermediate between gun-cotton and gun-cotton mixed with nitro (see table). Mixed with potassium chlorate it should develop more force than any other solid explosive substance.

*Temperature of Explosion.*—The temperatures required for the detonation of various explosive compounds have been determined by Leagué and Champion (*Compt. rend.* lxxiii. 1478), with the following results:—

Priming powder for Chassepot . . . . .	191
Fulminate of mercury . . . . .	200
Powder formed of potassium chlorate 1 part, sulphur 1 part. . . . .	200
Abel's protoxide (paper-pulp) . . . . .	205
Gun-cotton . . . . .	220
Powder formed of antimony sulphide 1 part, potassium chlorate 1 part . . . . .	280
Shooting powder . . . . .	283
Gunpowder . . . . .	295
Picrate of mercury . . . . .	} detonate at . . . . . 296
Picrate of lead . . . . .	
Picrate of iron . . . . .	
Picrate powder for torpedoes . . . . .	315

Picrate musket-powder . . . . .	358
Picrate gunpowder . . . . .	380
Artificial saffron . . . . .	315
Picric acid, picrate of magnesium, of ammonium, of potassium . . . . .	336
Nitroglycerin detonates at . . . . .	256-257
Inflammation of sulphur in the air . . . . .	246

L. Blekrode (*Phil. Mag.* [4], xvi. 39) finds that a flame may be applied to gun-cotton which has been previously wetted with carbon sulphide, without explosion taking place. Only the latter substance takes fire immediately, the gun-cotton remaining apparently intact amidst the burning sulphide, presenting almost the aspect of a mass of snow slowly melting away. Ether, alcohol, and benzene may be employed with the same result. Blekrode regards this slow combustion, which takes place when the cotton is moistened with carbon sulphide or any other volatile liquid, as a most direct and satisfactory proof in favour of the conclusion to which Abel was led by his researches, viz., that if the gases resulting from the first action of heat on gun-cotton upon its ignition in open air, are impeded from completely enveloping the burning extremity of the gun-cotton twist, their ignition is prevented; and as it is the comparatively high temperature produced by their combustion which effects the rapid combustion of the gun-cotton, the momentary extinction of the gases, and the continuous extraction of heat by them as they escape from the point of combustion, renders it impossible for the cotton to continue to burn otherwise than in a slow and imperfect manner, undergoing a transformation similar in character to destructive distillation. A piece of phosphorus placed in the moistened mass of gun-cotton, is melted and even boils during the combustion, but does not burn, as it is prevented from coming in contact with the oxygen till all the gun-cotton has disappeared. Blekrode suggests that gun-cotton should be preserved under carbon sulphide or benzene, to obviate the danger in case of fire. Should the liquid become ignited the cotton will be only slowly destroyed.

*Dependence of Explosion on Vibration.—Transmission of Explosion at a Distance.*—Champion A. Pollet (*Compt. rend.* lxxv. 110) have made a series of experiments with the object of following out Abel's theory, that for the explosion of detonating compounds a certain kind of mechanical excitement is necessary, the nature of which depends on the nature of the compound itself (*1st Suppl.* 487). These experiments tend to show that, at least in certain cases, the heat and the shock of an explosion at a distance operate in producing a second explosion, only by producing a certain vibratory motion, which may also be obtained by other means.

The first experiments tried were on explosions produced by means of a previous explosion at a distance. The detonator employed was iodide of nitrogen, which was found particularly suitable for delicate experiments. A tube, at first over two meters, and afterwards seven meters long, was constructed of two lengths joined together by a paper band. Small quantities of the iodide were placed at each end, and it was found that an explosion produced at one end of the tube immediately caused the explosion of the iodide at the other end. A pith-ball pendulum suspended within the tube remained quite motionless, showing that the second explosion was not caused by the pressure of the air in the tube, due to the sudden production of gas by the first explosion. If the tubes are not joined together by the paper band, but separated by an interval of five or six millimeters, the second explosion is not produced, or can be obtained only by using a comparatively large quantity of the iodide for the first explosion.

Experiments were also tried on producing explosion by means of other kinds of excitement. Iodide of nitrogen was fastened by means of a morsel of gold-beater's skin to the strings of a double-bass. It was found, on bowing the strings, that the iodide which was placed on the two lower strings did not explode, while that placed on the string giving the highest note exploded. The lowest number of vibrations that would produce an explosion was found to be about 60\* per second.

Experiments on the vibrations of metallic plates and of two small Chinese gongs yielded similar results: vibrations which gave deep sounds had no effect; but those giving the higher sounds readily produced an explosion.

The experiments above described illustrate the effect of vibrations in causing explosion of a detonator. The following show that heat, unless it is accompanied with mechanical vibrations of the proper kind, does not readily produce explosion.

Iodide of nitrogen was placed at the focus of a parabolic-mirror, and at the focus of a second similar mirror, nitroglycerin, fulminate of mercury, and gunpowder were ex-

\* According to ordinary English reckoning, 30 per sec. The French count half vibrations instead of complete vibrations from one end of the range to the other, and back again.

ploded. The results showed that, to cause the explosion of the iodide of nitrogen in the other focus, as much gunpowder was required as would produce ten times the heat given out in the burning of the required quantity of nitroglycerin. The mirrors were afterwards covered with lamp-black, and then even this large quantity of powder would not cause the iodide of nitrogen to explode. On the other hand, the lamp-black covering did not in the least prevent the nitroglycerin in one focus from exploding the iodide of nitrogen in the other.

A further set of experiments was made to determine the difference between the vibratory motions excited by various detonants, and thus to account for the difference in their power of causing by means of the intervening air, the explosion of other detonants placed at a distance. For this purpose a series of sensitive flames was arranged corresponding with the complete scale of  $g$  major, care being taken to tune the flames exactly to the proper pitch. Small quantities of various detonants were then exploded at small distances from the flames. In the case of iodide of nitrogen and mercuric fulminate, 0.03 gram of each being exploded; the former produced no effect upon the flames, while excitement of the flames,  $c, c, c, f, g$ , was noticed on the explosion of the latter. This seems to show that the vibrations excited by the two explosions are very different, and that the vibrations excited by mercuric fulminate act on the flames belonging to some notes of the scale to the exclusion of others.

Secondly, exploding these bodies at a shorter distance from the flames, it was found that, while the iodide of nitrogen affected the flames corresponding with the higher notes of the scale and those only, the mercuric fulminate acted on all the flames. Two-tenths of a grain of iodide of nitrogen placed at a short distance from the flames was found to influence them all.

The above experiments seem also to indicate, from the difference observed with the same amount of the same detonant placed at different distances, that acute sounds predominate in explosions.

The flames above described were not affected by the explosion of nitroglycerin, nitroethyl, nitroerythrite or nitrodulcitol. It is probable that this negative result was due to the small range of the apparatus, and that by constructing a set of flames graver than those employed in these experiments, the upper sounds of the explosion due to these bodies might be reached (*Compt. rend.* lxxv. 712).

The transmission of detonation through the agency of tubes has lately been made the subject of an elaborate series of experiments by Abel (*Proc. Roy. Soc.* xxii. 160—171), in which the explosive agents used were less highly susceptible, and more uniform and constant in composition than iodide of nitrogen, such as gun-cotton in different mechanical conditions, dynamite, mercuric fulminate, and preparations containing the latter as an ingredient.

The following are some of the points established by these experiments:—

1. The distance to which detonation may be transmitted through the agency of a tube to a distinct mass of explosive substance is regulated by the following conditions:

(a) by the nature and the quantity of the substance employed as the initiative detonator, and by the nature of the substance to be detonated, but not by the quantity of the latter, nor by the *mechanical condition* in which it is exposed to the action of the detonator.

(b) by the relation which the *diameter* of the 'detonator,' and of the charge to be detonated, bear to that of the tube employed;

(c) by the strength of the material composing the tube, and the consequent resistance which it offers to the lateral transmission of the force developed at the instant of detonation;

(d) by the amount of force expended in overcoming the friction between the gas and the sides of the tubes, or other impediments (such as loose tufts of cotton-wool) introduced into the latter;

(e) by the degree of completeness of the channel, and by the positions assigned to the detonator and the charge to be detonated.

2. The nature (apart from strength or power to resist opening up, or disintegration) of the material composing the tube through which detonation is transmitted, generally appears to exert no important influence upon the result obtained. At any rate the differences with respect to smoothness of the interior of the tubes far outweigh those which may prove traceable to differences in the nature of the materials composing them.

In the tube experiments with gun-cotton, many instances occurred in which the mass operated upon was *exploded*, but with comparatively little, if any, destructive effect, portions of the gun-cotton being at the same time dispersed and occasionally inflamed. Similarly, the mercuric fulminate was frequently exploded, through the agency of a transmitted detonation, in a manner quite distinct from the violent detona-

tions at other times developed. Even silver fulminate which, under all ordinary circumstances, detonates violently, and even when only one particle of a mass is subjected to a sufficient disturbing influence, was on one or two occasions exploded by the transmitted effect of a detonation of mercuric fulminate without the usual destructive action.

The dilution of a liquid and of a solid explosive body by inert solid substances produces very different results on the susceptibility of the compound to detonation. If the dilution does not affect the continuity of the explosive body, as when an explosive liquid, like nitroglycerin, is diluted with an inert solid, there appears to be no loss of sensitiveness to detonation; but if the continuity of the explosive be interrupted, as happens when a solid explosive is mixed with an inert body, the susceptibility to detonation is much diminished if the mass is loose and unconfined; but by compressing the diluted explosive, or strongly confining it, detonation may be much more easily produced. Thus mixtures of gun-cotton with potassium chloride, or still better with the chlorate or nitrate of potassium compressed with addition of water and then dried, were found to be more susceptible to detonation by nitroglycerin than undiluted gun-cotton itself.

The dilution of a solid explosive by a liquid greatly reduces its sensitiveness to detonation. Damp gun-cotton can be exploded only by large charges of mercuric fulminate; it is, however, much more easily exploded by an initiative detonator of dry gun-cotton.

Gun-cotton made up into a pulp with water is not susceptible of detonation, even by dry gun-cotton, unless the escape of force be retarded at the instant of the first detonation; but if this condition be fulfilled, either by the resistance of the material of the case, or by the pressure of a considerable column of water, the detonation may be accomplished with certainty. By confining the gun-cotton lightly in sheet-tin cases or bags, or even in fishing nets, and sinking it to a sufficient depth under water, or by placing the pulp in a shell and filling up the interstices with water, the whole can be detonated with a small charge of dry gun-cotton. Remarkable results were likewise obtained by detonating small charges of compressed gun-cotton in shells filled up with water. A quarter of an ounce of compressed gun-cotton detonated in a shell filled with water, broke it up into nearly eight times the number of fragments obtained by exploding a shell of the same kind full of gunpowder (13 oz.)

*Velocity of Transmission of Detonation.*—A series of experiments, in which the time was measured by Noble's electric chronograph, showed that with dry compressed gun-cotton the rate of transmission is between 17,500 and 20,000 feet per second when the masses are arranged so as to touch one another. The separation of the masses retards the transmission to an extent depending on the size of the masses and the distance between them. When gun-cotton saturated with water was employed, a marked increase in the rate of transmission was observed. Nitrated gun-cotton gave a slower rate, 15,500 to 16,000 feet per second. Dynamite, in continuous masses, gave 19,500 to 21,600 feet per second; but separation of the masses reduced the rate to a greater extent than was the case with gun-cotton. Nitroglycerin, contained in V-shaped troughs, gave a velocity of only 5,500 feet per second.

*New Class of Explosives.*—A class of explosives which are non-explosive during manufacture and transport has lately been introduced by Dr. Sprengel (*Chem. Soc. J.* [2], xi. 796). These explosives are mixtures of a combustible and an oxidising substance which can be kept separate during transport and mixed only when required for use. The examination of a considerable number of such mixtures showed that the most effective were mixtures of nitric acid, sp. gr. 1.5, and nitro-compounds of the hydrocarbons, fired by a detonating cap. A mixture of nitrobenzene or picric acid with nitric acid explodes with the greatest violence, comparable with that of the explosion of nitroglycerin. Porous cakes of potassium chlorate saturated with a combustible liquid, such as carbon sulphide or nitrobenzene, were found to be five times as effective in open granite quarries as an equal weight of gunpowder.

Experiments on the composition and tension of the products of combustion of gunpowder, when fired in a closed vessel, and in the bore of a gun, have lately been published by Captain Noble and Mr. Abel (*Proc. Roy. Soc.* liii, 1874). See GUNPOWDER.

## F.

**FAHL-ORE.** The separation of copper-pyrites and copper-glance from the fahl-ore of Wohlfach has been observed by F. Sandberger (*Jahrb. f. Mineralogie*, 1869, 301), who shows by calculation how this fahl-ore yields, in addition to the two minerals just mentioned, zinc-blende, brittle silver ore, and stibnite, which also occur at Wohlfach in a manner indicating the probability of their formation from the fahl-ore. The weathering of this same fahl-ore yields antimony-bloom coloured yellow by stibnite, besides a brown-red mass not yet examined.

**Bismuth fahl-ore.**—Analyses of two specimens of this mineral have been published by Petersen (*Jahrb. f. Mineralogie*, 1870, 464, 590): A. From Neubulach in the Württemberg Schwarzwald, in crude lumps intimately intergrown with the quartz gangue, and only once found crystallised in the form  $\frac{O}{2} \cdot \frac{2O_2}{2} \cdot \infty O$ ; sp. gr. = 4.908; analysed

by R. Senfter. B. Occurring with heavy spar and quartz at Cromez in the Emmenthal (Val d'Auniviers) in the canton Wallis; analysed by Brauns, who names it *Rönite*. The quantities of the metals found by analysis require only 25.13 p.c. sulphur. Petersen found 26.67 p.c., which he regards as too high, because copper pyrites is mixed with the mineral too intimately to allow of complete separation. Petersen is therefore inclined to refer the analysis to the general formula  $3RS.RS^3$ , which he regards as the typical formula of the fahl-ores:—

	S	As	Sb	Bi	Cu	Ag	Pb	Zn	Fe	Co	Ni	
A.	24.85	13.63	4.28	6.33	41.13	trace	1.52	3.82	3.74	trace	trace	= 99.50.
B.	29.10	11.44	2.19	13.07	37.52	0.01	—	—	6.51	1.20	—	= 101.07.

**FAT.** *The Storing up of Fat in the Animal Organism.*—Experiments have been made by F. Hofmann (*Zeitschr. f. Biologie*, viii. 153) to determine in what way fat becomes deposited in the body, whether it is derived directly from the fatty elements of the food, or whether, as Toldt and Subbotin hold, it is derived from the splitting up of albuminoids; or whether, according to the views of Radziejewski, all fats must be first saponified, and again undergo synthesis into neutral fat in the organism. To this latter conclusion Radziejewski was led by his experiments on the feeding of animals with fats which do not normally exist in the body. Hofmann, however, is of opinion that Radziejewski's conclusions are much wider than his premises, as his experiments merely prove that foreign fats are not stored up. The same is shown by Subbotin's experiments with spermaceti.

Hofmann's method consisted in starving dogs till all the body-fat was used up, and then feeding them with large quantities of fat, mixed with as small a proportion as possible of lean meat. After a few days the animals were killed, and the whole quantity of fat in the body determined. The fat found was regarded first as that derived from albuminoids. If the quantity found is not greater than might possibly be derived from albuminoids, it is considered that all the fat of the food has been burnt and none deposited. If, on the other hand, a larger proportion of fat is found than can be accounted for in this way, it can only have come from the food. This would not, however, decide the question whether the fat was stored up in the cells, for it might exist in the blood. If, however, not more than usual is found in the blood, and an amount corresponding with the quantity absorbed is found, this quantity may be considered as fat really deposited in the tissues of the body.

The first point to determine was when the whole of the fat of the body had been used up by the process of starvation. Considerable differences in time are observed, according as the animal has or has not a large store of albuminoids, as well as fat, in its system. In general it is found that the fat of the body is almost entirely absorbed when the excretion of urea suddenly becomes greatly increased after a long period of starvation. This indicates that the wants of the organism require the combustion of a large amount of nitrogenous constituents to make up for the fat which has now disappeared.

A dog so starved was found capable of assimilating considerable quantities of fat when mixed with a small proportion of flesh. At the end of a few days, however, dyspeptic symptoms appeared, and almost pure fat was passed as excrement. This was attributed to the fatty condition of the liver which was induced. The animal in five days increased in weight more than 21 p.c. of its weight on the last day of starvation. This increase was shown not to be due to water alone, or to the small

amount of lean meat of the food. Analysis of the blood likewise proved that this did not contain more than the usual proportion of fat.

The whole amount of fat in the body was determined by thoroughly mincing the whole animal, and reducing all its tissues to a uniform mass. Fractional analysis of this mass gave uniform results, and allowed of easy estimation of the whole fat in the body.

The results show that in five days a dog had absorbed 1854.0 grams of fat. If 130.7 grams be taken as the amount derived from albuminoids, a total of 1984.7 grams represents what was used by the organism. The quantity found in the body by analysis was 1352.7 grams, giving 632.0 grams as the quantity which had undergone combustion. These figures show that a very large amount of fat may be absorbed from the food and deposited in the tissues. The deposit takes place principally in the liver and mesentery.

Hofmann questions whether it will be possible by the above method to determine whether fatty acids may undergo synthesis into fat, as it is impossible to give large quantities of soaps to animals without inducing serious derangement of the alimentary canal.

That fats are deposited in the organism, and not all burnt off, is also shown by the experiments of Pettenkofer and Voit, which prove that the amount of carbon given off by an animal receiving a large proportion of fat in its food is far below what would be required to cover the amount of fat consumed.

*Extraction and Purification of Fats.*—The following process is described by H. Pohl (*Dingl. polyt. J. sci.* 254):—

The fresh raw fat, freed as far as possible from fleshy matters, is cut into thin slices and washed free from blood, &c. with pure cold water. The washed fat is then placed in a cylindrical stoneware vessel about 4 feet high and 18 inches wide, standing in a water-bath which can be heated by steam. A cock of wood or stoneware at the bottom of this vessel enables it to be emptied without removal from the water-bath. After the cylinder has been three-fourths filled, a kind of sieve of stoneware is laid on the surface of the fat; 10 per cent. of pure highly diluted hydrochloric acid is added (3 lbs. acid of sp. gr. 1.12 to 100 lbs. water), and a well-fitting cover of stoneware is laid over the top. On warming, as the fat melts in the cells, the acid dissolves the membranous portions, and the sieve gradually sinks to the lower part of the cylinder, carrying with it the skinny matters and unmelted fat, while the pure melted portion collects in the upper part of the vessel. When all the fat is melted, the dilute acid solution is run off at the bottom, and the fat is washed two or three times with boiling water, to the last portion of which a little magnesium carbonate is added to ensure perfect naturalisation.

The washed fat is dissolved in an equal volume of Canadian oil, which separates a nitrogenous matter. The solvent is then recovered by distillation. The resulting fat is scentless and tasteless, almost colourless, and absolutely neutral. It contains no trace of water or of nitrogenous matter, and therefore remains free from all tendency to become rancid when kept.

The rancid odour which fats often acquire by keeping, arises from the presence of volatile fatty acids and other volatile products, which do not exist in the fresh fat, but are produced by decomposition. These substances may be removed by heating the fat to a certain temperature. According to Dubrunfaut (*Compt. rend.* lxxi. 37) fish-oils are entirely deprived of their odorous principle by simply heating them to 330°, and fatty acids distil over with steam when heated above 100°, whereas neutral fats are fixed under these conditions, but behave like the fatty acids when submitted to a current of steam at 300°–330°. When fat is melted in a frying-pan at 140°–150° and then cautiously sprinkled with water, the steam thus evolved carries off with it all the offensive matters, and leaves the fat sweet.

*Saponification.*—A method of saponification was described some years ago by Mège-Mouriès (*Compt. rend.* lviii. 864), depending on the property of fats in the state of emulsion (*état globulaire*) to take up soda-ley containing sodium chloride without dissolving in it. Melted tallow is brought into this state by heating it to 45° with a 5 to 10 per cent. of aqueous soap-solution; and if soda-ley containing common salt be then added, and the action promoted by assiduous mixing, the tallow is completely saponified at the same temperature in a few hours (2,000 kilo. in three hours). At a somewhat higher temperature, a little above 60° C. (140° F.), the globules of soap thus formed unite into a semi-fluid transparent layer, which floats on the salt-liquor containing glycerin; and by decomposing this layer with the exact quantity of dilute sulphuric acid required, and pressing the mixture of fatty acids thereby separated, stearic acid melting at 58°–59° is obtained, together with nearly colourless oleic acid. The process is said by its inventor to be recommended by the rapidity of the operation.



the beauty of the products, and the avoidance of loss (the product of fatty acids amounting to 96-97 p.c. of the calculated quantity). According to De Milly, on the other hand (*Dingl. polyt. J.* clxxvi. 145), this method of saponification is less advantageous than that commonly practised, being more costly and not yielding any glycerin. Legrand also (*ibid.* 151) finds it disadvantageous, at least for the manufacture of soaps, chiefly on account of imperfect combination of the fatty acids, and the consequent too great solubility and want of durability of the soap.

F. Knapp (*Dingl. polyt. J.* clxxx. 309) has obtained the following results in accordance with those of Mège-Mouriès. When melted tallow is triturated in a mortar with starch-paste and water, a uniform mobile emulsion is formed, from which on standing the tallow separates on the surface as a creamy layer. On freeing it from adhering starch-paste by agitation with water, the milky mixture appears under the microscope as an aggregate of very small, globular, transparent bodies, with somewhat ragged surface and having usually a diameter not exceeding that of the starch-granules of leguminous fruits. Tallow in the form of this emulsion is quite permanent. When diffused in soda-ley, either concentrated or dilute (3 p.c.), it forms in a few hours at 45°-60°, in a somewhat longer time at ordinary temperatures, a coherent floating layer of soap, small quantities of unsaponified fat remaining however enclosed in it. Microscopic examination shows that a rapid interchange of constituents is going on between each individual globule of tallow and the surrounding ley, and that the attack of the ley, even when it is rather concentrated and therefore forms a soapy envelope round each granule of tallow, nevertheless penetrates by diffusion into its interior. The easy and rapid saponification of fats in the utricular state depends therefore on their microscopic division; it takes place in the same manner in ethereal solutions, and instantly in liquids containing fat, alkaline-ley, and soap uniformly dissolved, or when the base employed forms, not a gelatinous, but a pulverulent or flocculent soap. In the ordinary soap-boiler's process, the fat is likewise emulsified at the beginning, and almost completely saponified by prolonged contact in the cold with the alkaline-ley; and if the saponification afterwards proceeds but slowly when heat is applied, this arises from the circumstance that the soapy envelopes melt the individual fatty globules, and thus destroy the minute division of the fat. The further action is then brought about chiefly by the solubility of the fats in the hot soap already formed. It appears therefore advantageous in all cases that the fat emulsified by the alkaline ley should first be left to itself for some time at a moderate heat.

Further experiments by Knapp (*Dingl. polyt. J.* xcii. 198) have led to the following results: The soap produced from emulsified fats by digestion in the cold, separates on the surface of the liquid in the form of a cake, which, according to the strength of the ley employed, is sometimes lurd and brittle, sometimes soft and more or less hydrated. After repeated rinsing the cakes do not dissolve completely in boiling distilled water, but a few drops of the alkaline-ley suffice to render the turbid boiling liquid perfectly clear. Cakes prepared from tallow dissolve completely in warm strong alcohol, after the subjacent liquid has been saturated with carbonic acid, with exception of a residue of sodium carbonate. The filtered and evaporated soap-solution gives, on decomposition with sulphuric acid, a quantity of sodium sulphate equivalent to 11 p.c. of anhydrous sodium oxide, that is to say, an amount not differing much from that of ordinary soap, showing that the saponification is complete. In carrying out the process on the large scale, it would be necessary, after removing the excess of ley, to dissolve the soap-cake at the boiling heat, without previously rinsing it, so as to obtain a clear solution at once. For the preparation of the emulsion, mucilaginous substances, such as gum, would be too costly; soap is better adapted for the purpose, but the change is most advantageously effected by means of the caustic ley which serves for the saponification. It must be diluted with very pure water, which may be added to it in any quantity without producing turbidity, whereas water containing common salt, acids, &c., immediately causes the separation of white flocks which rise to the surface like a thick cream. Excess of ley must especially be avoided, as it drives the fat immediately to the surface. In saponifying solid fats, the containing vessel and the water must of course be raised to the melting points of the fats.

**Fat of Seeds and Fodder.**—The quantity and elementary composition of the fat of various seeds, and of hay, straw, &c., has been determined by J. König (*Landwirtschaftliche Versuchs-Stationen*, xiii. 241). The fat was extracted by ether, and in the case of drying oils which oxidise quickly, both the seed and the ethereal extract were dried in a stream of hydrogen. The ethereal extracts, except in the case of the oil-seeds, were freed from chlorophyll by means of animal charcoal. This treatment involves a slight loss, as the charcoal obstinately retains a small quantity of fat:—

TABLE A. *Quantity of Fat in Seeds, &c.* (König.)

	Fat per cent. in fresh substance	Fat per cent. in dry substance		Fat per cent. in fresh substance	Fat per cent. in dry substance
Linseed . . . .	31·94	35·21	Rye . . . . .	1·35	1·44
Rape seed . . . .	41·90	45·49	Wheat . . . . .	1·14	1·23
Hemp seed . . . .	32·37	35·25	Oats . . . . .	4·04	4·53
Poppy seed . . . .	40·07	43·39	Barley . . . . .	1·51	1·59
Beech-nut . . . .	23·08	28·18	Maize . . . . .	4·47	4·85
Palm-nut kernel . .	48·07	52·85	Lupino . . . . .	5·20	6·10
Earth-nut . . . .	51·51	55·25	Peas . . . . .	·81	·93
White sesame . . .	49·31	52·50	Beans . . . . .	·83	·96
Black sesame . . .	46·02	49·28	Grass hay . . . .	1·39	1·52
Cocoa-nut . . . .	64·48	67·76	Clover hay . . . .	1·43	1·61
Madia seed . . . .	37·32	40·44	Rye straw . . . .	·76	·83
Cotton seed . . . .	19·49	21·72	Oat straw . . . .	·81	·88

The fat obtained from the purified ethereal extract is, in the case of hay, a mixture of fat and wax. These may be separated with tolerable accuracy by dissolving the crude fat in hot absolute alcohol, the wax then separating on cooling; it is washed with cold alcohol, and weighed. Among the seeds examined, rye alone contained an appreciable amount of wax. Dry fodder gave the following percentages of fat and wax:—

TABLE B. (König.)

	Fat	Wax		Fat	Wax
Meadow hay (mean of five samples)	1·07	·45	Rye straw . . .	·52	·31
Clover hay . . . .	1·23	·38	Oat straw . . .	·55	·33
			Rye grain . . .	1·35	·09

The elementary composition of the various fats was determined from fats purified by treating their ethereal solution with animal charcoal. The lupine fat was further treated with hydrochloric acid, and again exhausted with ether, to separate the alkaloid which it contains. In table C (page 507), the fluid or solid nature of the fat is indicated by the letters *f* and *s*.

The percentage composition of the various fats agrees in most cases with that of a mixture of the three glycerides:—

Triolein . . . .	77·38 carbon.	11·76 hydrogen.	10·86 oxygen.
Tristearin . . . .	76·85 „	12·36 „	10·79 „
Tripalmitin . . . .	75·93 „	12·16 „	11·91 „

Rape oil gives an unusually high proportion of carbon; this arises from its containing the glyceride of brassic acid. Earth-nut fat apparently contains fatty acids low in the series, as the fats known to be present, namely, palmitin, arachin, and hypogæin, have all more carbon than was found on analysis. Palm-nut kernel fat is probably rich in some of the lower fatty acids, as indeed is suggested by its odour. Cocoa-nut fat is known to contain the glycerides of capric, caprylic, and caproic acids; the presence of these accounts for the low amount of carbon found. The specimens of oat, maize, and lupine oil had become somewhat oxidised by exposure to air. The oil of maize is apparently a drying oil.

The fats of the seeds of oats, rye, tares, and linseed, have been further examined by König, Kiesow & Aronheim (*Landw. Versuchs-Stationen*, xvii. 1). The fats were saponified with lead oxide to remove glycerin, &c.; the watery extract was evaporated; the lead plaster treated with ether to remove lead oleate; and the residual lead salts were decomposed with acid and extracted with ether to obtain the solid acids. By this treatment 100 parts of the several fats were found to yield:—

	Oats	Rye	Tares	Linseed
Oleic acid . . . .	60·5	91·6	96·31	102·8
Solid acids . . . .	36·7	8·1	2·11	·2
Soluble in water, glycerin, &c. . . .	2·8	1·3	1·6	

TABLE C. *Elementary Composition of Vegetable Fats.* (König.)

Consistence of fat	Source of fat	C.	H.	O.	Consistence of fat	Source of fat	C.	H.	O.
f	Linseed. . .	77.40	11.10	11.50	s	Cocoa-nut . .	74.16	11.72	14.12
"	Poppy seed. .	76.57	11.41	12.02	f	Rye . . . . .	76.71	11.79	11.50
"	Hemp seed. .	76.00	11.30	12.70	"	Wheat . . . .	77.19	11.97	10.84
"	Rape seed. . .	78.04	12.04	9.92	f/s	Barley . . . .	76.29	11.77	11.94
"	Boech-nut . .	76.65	11.47	11.88	f	Oats . . . . .	75.67	11.77	12.56
"	Madia seed . .	77.23	11.41	11.36	"	Maize . . . .	75.79	11.43	12.78
"	White sesame .	77.38	11.59	11.03	"	Lupine . . . .	75.94	11.59	12.47
"	Black sesame .	76.17	11.44	12.39	"	Peas . . . . .	76.71	11.96	11.33
"	Cotton seed . .	76.40	11.53	12.27	"	Beans . . . . .	77.50	11.81	10.69
s	Earth-nut . .	75.73	11.57	12.70	s	Potatoes . . .	76.17	11.85	11.98
"	Palm-nut kernel :—				"	Mangolds . .	76.12	11.69	12.19
f	(a, sol. in cold alcohol . .)	73.03	11.64	15.33	f	Rice meal . .	76.17	11.51	12.32
s	(b, little sol. in cold alcohol)	75.23	11.83	12.94					
Portion soluble in cold alcohol :—					Portion scarcely soluble in cold alcohol :—				
f	Meadow hay .	76.43	11.17	12.40	s	Meadow hay .	81.70	13.70	4.60
"	Clover hay . .	77.14	12.78	10.08	"	Clover hay . .	82.50	13.26	4.21
s	Rye straw . .	77.39	12.30	10.31	"	Rye straw . .	80.17	12.46	7.37
"	Oat straw . .	78.60	12.30	9.01	"	Oat straw . .	83.54	13.85	2.61
"	Pea straw . .	79.29	12.77	7.94	"	Pea straw . .	83.51	14.24	2.25

No glycerin could be detected in the first three fats, and the quantity of solid acids in linseed oil was but small. The elementary composition and melting point of the solid acid indicated in each case a mixture of palmitic and stearic acids. The acids in the fat of oats, rye, and tares, must be present almost entirely in the free state, a small portion being probably combined with cholesterin; and linseed oil must contain a considerable proportion of free acid, as 5.2 p.c. glycerin is equivalent to only 42.7 p.c. of linoleic acid, if present as trilinoleate.

The fat of meadow hay extracted by ether may be separated by cold alcohol into a fluid soluble portion, and a solid waxy matter which is insoluble. Both these fats saponify in great part when treated with alcoholic potash; and the resulting soaps decomposed in the usual way, yield cerotic, palmitic, and oleic acids.

The unsaponified portion of the waxy matter heated with benzoic acid to 200° in a sealed tube for several hours, is resolved into a hydrocarbon and the benzoic ethers of several fatty alcohols, viz. ceryl alcohol ( $C^{27}H^{56}O$ ), an alcohol of the same species, probably  $C^{25}H^{52}O$ , cholesterolin ( $C^{26}H^{54}O$ ), and a fluid alcohol  $C^{20}H^{40}O$ , which forms with benzoic acid an ether liquid at ordinary temperatures and easily soluble in absolute alcohol; the fluid alcohol is readily oxidised by chromic acid mixture to acetic acid and an acid which melts at 20° and contains 73.57 p.c. carbon and 12.41 hydrogen. The hydrocarbon gave by analysis 84.96 p.c. carbon and 15.28 p.c. hydrogen, agreeing most nearly with the formula,  $C^{20}H^{42}$ , but not improbably consisting of cerotic  $C^{27}H^{54}$ .

The fat of oat straw contains the same acids as that of hay. The portion soluble in alcohol contains the same fluid and solid alcohols as hay-fat but not the hydrocarbon (König u. Kiesow, *Landw. Versuchs-St.* xvi. 47; *Deut. Chem. Ges. Ber.* vi. 500, König, Kiesow u. Aronheim, *loc. cit.*)

On the Digestibility of the Fat of Meadow Hay, see E. Schulze (*Landw. Versuchs-St.* xv. 81; xvi. 329; *Chem. Soc. J.* [2], x. 1037; xii. 85).

On the Influence of the Addition of Fat to the Food on its Digestibility, see Hofmeister (*Landw. Versuchs-St.* xvi. 347; *Chem. Soc. J.* [2], xii. 83).

**FATTY ACIDS.** *Occurrence in Wood Vinegar.*—According to Barré (*Compt. rend.* lxxviii. 1222), the crude acid obtained by the dry distillation of wood, contains, besides acetic acid, small quantities of formic and larger quantities of propionic,

butyric, valeric and caproic acids, these latter separating as an oily layer on adding sulphuric acid to the difficultly crystallisable mother-liquor of the sodium acetate.

In *Hungarian Fusel-oil*.—A sample of wine fusel-oil from Pesth having a dark hock colour and a strong nauseous odour, when freed by distillation from water, ethyl alcohol and amyl alcohol, left an acid residuo (a little more than half the original liquid) which was found to contain capric acid together with a little caprylic and perhaps ceananthylic acid; no pelargonic acid (Grimm. *Ann. Ch. Pharm.* elvi. 264).

For the mode of separation see CAPRIC ACID (p. 249). The same acids were found by Fischer in crude ceananthic ether (iv. 174). Capric acid has also been found by Rowney in the fusel-oil of the Scotch distilleries (ii. 753).

*Preparation from the Soapy Waters obtained in the washing of Wool*.—These wash-waters are acidulated with sulphuric acid—on the average 50 lbs. sulphuric acid of 66° Bm. to 7,000 litres of liquid. The separation of the fatty acids is facilitated by warming. The fatty mud thus obtained, containing on the average 400 lbs. of solid matter to 7,000 litres of water, is pressed after draining off the water, first while cold then when hot. The quantity of fat thus expressed amounts to only 100 lbs. to 7,000 litres of water, while 200 lbs. of the mud remains as press-cake. The fat is clarified by boiling with dilute sulphuric acid and subsequent washing with water, and bleached by treatment with potassium chlorate or with potassium chromate and sulphuric acid. The mixed product of solid and liquid fat may be used as such for soap-making; or it may be separated, by slow cooling after fusion, into the solid and liquid portion, and the two used separately for lubrication, soap-making, &c. The press-cake still contains 34.74 p.c. fat and 22.37 p.c. of other organic substances; it is said to be applicable chiefly for gas-making (Märker u. Schulze, *Dingt. polyt. J.* excv. 173).

*Preparation of solid fatty acids without distillation*.—Solid fatty acids may be prepared in a short time without distillation, by treating neutral fats with 2 p.c. of sulphuric acid. The black mass thereby formed is soluble in oleic acid and may be separated, together with this latter, by pressure. If the fatty substances be mixed with water, the addition of the acids produces at first a slight coloration which afterwards disappears; and if the addition of acid be continued till the colour becomes permanent, a solid perfectly white mass separates, from which the acid may be separated by decantation. Further addition of acid and heating converts this solid mass into charcoal, no longer soluble in the fatty bodies, which melt and float on the water (Bouis, *Deut. Chem. Ges. Ber.* ii. 79).

**FELSPAR.** *Orthoclase and Albite*.—The following analyses of these minerals from the granites of Scotland are given by S. Haughton (*Phil. Mag.* xl. 59). a.-d. *Orthoclase*; a. From Stirling Hill, Peterhead: sharp opaque flesh-coloured crystals with a coating of albite. b. From Rubislaw, Aberdeen: flesh-coloured opaque crystals associated with white mica, from a granite not containing albite, which in contradistinction to the eruptive granite of Stirling Hill, is designated as 'metamorphic.' c. Peterculter, Aberdeen: large white transparent crystals from 'metamorphic' granite. d. Callernish on the west coast of Lewis: large grey crystals with a tinge of flesh-colour from metamorphic granite. e. *Albite*: clearly translucent, spotted on the surface with ferric oxide; occurs as a coating on the orthoclase a.

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	CaO	MgO	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O	
a.	65.40	19.04	trace	0.22	trace	3.63	11.26	0.20	= 99.75
b.	64.44	18.64	0.80	0.66	trace	2.73	12.15	0.80	= 100.22
c.	64.48	20.00	—	1.01	trace	1.72	12.81	0.64	= 100.66
d.	64.48	20.00	—	0.78	—	2.19	12.10	0.08	= 99.63
e.	68.00	20.00	—	0.35	trace	10.88	0.68	—	= 99.91

*Albite and Orthoclase from Harzburg*. (A. Streng, *Jahrbuch f. Mineralog.* 1871. 715.)—These two minerals occur in the graphic granite of the Radautal, near Harzburg. The albite is found—1. Crystallised in druses, mostly implanted on orthoclase in parallel rows. 2. Imbedded in the orthoclase in distinct layers, partly parallel to  $\alpha P$ , partly to  $\alpha P\infty$ . 3. Intergrown with orthoclase in lamellæ, recognisable only by the microscope, the lamellæ being partly parallel to  $\alpha P\infty$ , partly to  $(\alpha P\infty)$ . 4. As an independent constituent of the graphic granite, but in this case also intergrown with small quantities of orthoclase. Thin slices of both minerals, when examined by the microscope, are seen to be interspersed with very minute, blue or greyish-blue, granular, and extremely thin brown-red lamellæ of some foreign mineral or minerals. The lamellæ probably consist of iron-glance or mica.

The albite crystals are mostly twins, having their axis of combination perpendicular to the brachypinacoid  $\alpha P\infty$ , very rarely parallel to the principal axis. Simple crystals are, however, also found, not exhibiting any re-entering or projecting

edges. The crystals are mostly combinations of the faces  $\infty P'$ ,  $\infty P$ ,  $\infty P_3$ ,  $\infty P_3$ ,  $\infty P$ ,  $\infty P$ ,  $\infty P$  (occurring as a truncation of the acute edge of  $P'$ :  $\infty P$ ,  $\infty P$ ,  $\infty P$ , and  $P$ ).

The faces  $\infty P$  and  $\infty P$  are mostly predominant, the prismatic faces subordinate, sometimes, however, equally developed with the other faces. The eight prismatic faces are never present altogether. The crystals are white to colourless, have a strong lustre, and are translucent to transparent. Sp. gr. = 2.600 at 12°.

The analysis of this albite showed that it is a mixture 20 mol. pure albite (sodic feldspar), and 1 mol. anorthite (calcic feldspar), or 94.85 p.c. albite and 5.15 anorthite.

	Calc.	Found	Or:		Calc.	Found
SiO <sub>2</sub> . . .	67.40	67.75		Si . . .	31.69	31.86
AlPO <sub>3</sub> . . .	20.43	18.42		Al . . .	10.92	9.85
Fe <sub>2</sub> O <sub>3</sub> . . .	—	2.08		Fe . . .	—	1.52
CaO . . .	1.03	0.92		Ca . . .	0.74	0.66
MgO . . .	—	0.14		Mg . . .	—	0.08
K <sub>2</sub> O . . .	—	0.38		K . . .	—	0.32
Na <sub>2</sub> O . . .	11.14	11.81		Na . . .	8.26	8.76
	100.00	100.00				

The orthoclase occurs in drusy cavities of the graphic granite, in crystals from 1 to 2 inches long, and of simple form, exhibiting mostly only the prismatic face  $\infty P$  and the three pinacoids.  $P$  is rarely visible. The mineral is greyish white, opaque, and dull. Analysis gave—

	SiO <sub>2</sub>	AlPO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	
Or,	65.21	20.40	1.04	0.55	0.06	9.27	4.77	= 101.40
	Si	Al	Fe	Ca	Mg	K	Na	O
	30.66	10.91	0.81	0.39	0.04	7.78	3.51	47.37 = 101.40.

These numbers give—

$$R^2R^3 : R^1 : Si = 1 : 1.15 : 5.84,$$

showing that the orthoclase in question is very impure, since for pure orthoclase the ratio is 1 : 1 : 6. If the impurities be regarded as iron-glance, and the iron be accordingly left out, the ratio becomes 1 : 1.07 : 5.84, which does not differ much from that of pure orthoclase. The ratio of the alkalis and alkaline earths shows that the mineral is a mixture of about 6 molecules of pure orthoclase with 5 molecules of a sodio-calcic feldspar containing but a small proportion of calcium.

The mineral from the augitic granite of the Radanthal described by Fuchs (*Leont. Jahrb.* 1862, 789) as oligoclase, and containing 65.83 p.c. SiO<sub>2</sub>, 20.46 AlPO<sub>3</sub> with a trace of Fe<sub>2</sub>O<sub>3</sub>, 0.71 CaO with trace of MgO, 6.94 K<sub>2</sub>O, and 5.89 Na<sub>2</sub>O, appears rather to be an albite rich in potash, since the proportion of lime is much too small for oligoclase.

Orthoclase from Elba, in which G. vom Rath found 3.40 p.c. Na<sub>2</sub>O to 11.93 K<sub>2</sub>O, was also found by Streng, on microscopic examination, to be intersected by lamellæ and small crystals of albite.

The following orthoclases and mixed orthoclasic feldspars have been described and analysed by G. vom Rath (*Jahrb. f. Mineralogie*, 1870, 890; *Pogg. Ann.* cxliv. 375, 594).

(1). *White or Yellowish Orthoclase from S. Piero in Elba.*—Characteristic forms:  $\infty P$ .  $\infty P$ .  $\infty P_3$ . and  $\frac{1}{2}P$ . The crystals are mostly simple, but twins likewise occur. Interposed laminae of albite give the crystals the appearance of perthite, and produce peculiar phenomena of weathering, resulting in a corroded appearance. Selected material was used for analysis since the orthoclase is usually intergrown with quartz in the manner of graphic granite. Sp. gr. = 2.540; after ignition (loss 0.39 p.c.), 2.515; after repeated ignition at a higher temperature, 2.506.

SiO <sub>2</sub>	AlPO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
64.64	19.40	11.95	3.40 = 99.39

This feldspar was found by Streng (*loc. cit.*), on microscopic examination, to be intersected with lamellæ and small crystals of albite.

(2). *Orthoclase from Bolton in Massachusetts.*—This mineral is accompanied by large crystals of green augite and brown titanite. The surface of the crystal is rough, drusy, and of a yellowish colour, the interior pure white, semi-transparent. The

cleavage faces  $OP$  and  $(\infty P\infty)$  are slightly curved, but without any trace of twinning or albite lamellæ; colour and lustre similar to those of adularia. Sp. gr. 2.586. Loss by ignition 0.05 p.c.

A very similar feldspar, accompanied by fine crystals of augite, scapolite, and titanite, is found in the neighbourhood of Diana, Lewis City, New Jersey.

(3). *From Pargas in Finland*, also accompanied by augite. The crystals are sometimes 2 centimeters long, but mostly much smaller. They are white, and covered with a dull white crust of milky aspect. The edges are rounded. Sp. gr. 2.576. Loss by ignition 0.13 p.c.

	$SiO_2$	$Al_2O_3$	$CaO$	$MgO$	$K_2O$	$Na_2O$
(1). . .	64.64	19.40	—	—	11.95	3.40 = 99.39
(2). . .	65.23	19.26	0.42	—	11.80	2.98 = 99.69
(3). . .	64.96	19.40	0.49	0.25	12.80	2.32 = 100.22

All three analyses agree nearly with the composition of an orthoclase containing 3 at.  $K$  to 1 at.  $Na$  (or a mixture of 3 mol. potash feldspar to 1 mol. albite), which requires 65.58  $SiO_2$ , 18.73  $Al_2O_3$ , 12.87  $K_2O$ , and 2.82  $Na_2O$ .

The two following orthoclasic feldspars exhibit abnormal composition, and should perhaps be regarded as mixtures of orthoclase, albite, and anorthite.

(4). *Feldspar from the Syenite of Laurvig.*—This mineral is the principal constituent of the remarkable rock which extends along the coast of Norway from the Langesund fjord to the Christiania fjord. The crystals are bluish to brownish grey, and exhibit a composite structure. A thin section parallel to  $OP$  appears, even by ordinary light, as an intimate combination of curved lamellæ, exactly like the intergrowth of orthoclase and albite exhibited in perthite. In polarised light this striation of the surface is much more evident, the lamellæ which are inserted nearly parallel to the orthopinacoid exhibiting a variety of brilliant colours. Sp. gr. 2.619. Loss by ignition 0.31. Analysis gave numbers agreeing approximately with a mixture of 1 mol. orthoclase, 3 mol. albite, and 2 mol. anorthite:—

	$SiO_2$	$Al_2O_3$	$CaO$	$MgO$	$K_2O$	$Na_2O$
Analysis . .	62.81	23.21	2.60	0.07	4.23	7.54 = 100.46
Calculation .	62.48	22.94	4.16	—	3.50	6.92 = 100

(5). *Feldspar from the Syenite of Monte Monzoni* (Toul, near Rizzoni), Fassa. — This feldspar forms the predominating constituent of the beautiful coarse-grained syenite which in some places may be regarded as of more or less pure feldspathic constitution. The light-grey feldspar occurs in grains  $\frac{1}{2}$  to 2 centimeters in diameter, together with small quantities of black hornblende and a very few small granules of titanite. Microscopic examination in polarised light showed that this feldspar also contained a quantity of small grains of plagioclase imbedded in its substance. No striation was, however, visible, the granules of plagioclase being merely intergrown with the orthoclase in parallel directions, but otherwise irregularly. Sp. gr. 2.665. Loss by ignition 0.89 p.c. (the mineral splits when ignited).

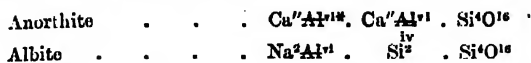
Analysis gave the following numbers, agreeing closely with the composition of a mixture of 5 mol. orthoclase, 4 mol. albite, and 2 mol. anorthite:—

	$SiO_2$	$Al_2O_3$	$CaO$	$K_2O$	$Na_2O$
Analysis . .	63.36	21.18	1.66	8.89	4.91 = 100
Calculation .	63.96	20.78	2.06	8.65	4.55 = 100

The somewhat considerable quantity of lime is accompanied, as in the Laurvig feldspar, by an increase in the proportion of alumina and a decrease in that of the silica, which is in accordance with the supposition that the plagioclase mixed with these feldspars is a mixture of albite and anorthite. Other orthoclasic feldspars, loxoclase for example, containing lime with a large proportion of soda, are probably constituted in a similar manner.

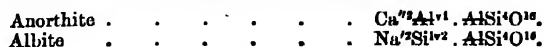
*Triclinic (sodio-calcic) Feldspars.*—These feldspars, viz., albite, oligoclase, andesine, labradorite, and anorthite, form an isomorphous group, the end-terms of which are albite and anorthite, the former being a pure soda-feldspar, the latter a pure lime-feldspar, whilst the others are isomorphous mixtures of these two, approximating in physical properties and chemical composition to the one or the other according as the soda or the lime predominates. This view, first suggested by Sartorius v. Waltershausen (*Ueber die vulkanischen Gesteine in Sicilien u. Island*, 1853), and further developed by Tschermak (*Wien. Akad. Ber.* 7 [1 abth.], 566; *Jahresb.*, 1865, 888), has lately been corroborated by the observations of Streng (*Jahrb. f. Mineralogie*, 1871, 598 and 715) and of G. vom Rath (*Pogg. Ann.* cxliv. 210).

Streng observes that the composition of albite and anorthite may be represented as follows:—



the atomic group  $\text{CaAl}$  in anorthite being equivalent to the group  $\text{NaAl}$  in albite, and the second group  $\text{CaAl}$  in the former to  $\text{Si}^2$  in the latter.

The formulæ of the two minerals may also be written as follows:—



The general formula of a sodio-calcic feldspar may then be written in the form  $\text{Na}^{2n}\text{Si}^{2n}\text{Ca}^{2-2n}\text{Al}^{1-n}\text{AlSi}^{\text{iv}}\text{O}^{16}$ , in which  $n$  is a fraction intermediate between 0 and 1, whose denominator shows the number of molecules of albite which are present in the number of molecules of any other triclinic feldspar denoted by the numerator.

These formulæ must not be looked upon as constitutional formulæ, but merely as indicating that equivalent groups  $\text{Ca}^2\text{Al}$ ,  $\text{Na}^2\text{Si}^2$ , play an analogous part in the two compounds. Analysis shows indeed—and this is the chief chemical argument in favour of the theory—that an increase in the proportion of lime in a sodio-calcic feldspar is attended with an increase of the alumina and a decrease of the silica, while, on the other hand, an increased proportion of soda is attended with a diminution of the alumina and an increase of the silica; also that a definite proportion of lime to soda corresponds in all cases with a definite amount of silica.

The crystallographic differences between the three most important members of the series of sodio-calcic feldspars, viz., albite, oligoclase, and anorthite, are shown in the following table, in which

$c$ denotes the principal axis	} in the right upper octant.
$A$ the inclination of the axial planes $ab, ac$	
$B$ " " " $ab, bc$	
$C$ " " " $ac, bc$	
$\alpha$ the angle between the axes $b, c$	
$\beta$ " " " $a, c$	
$\gamma$ " " " $a, b$	

$a : b : c$	A	B	C	$\alpha$	$\beta$	$\gamma$
<i>Albite.</i>						
0.6284 : 1 : 0.5556	93°36'	116°18'	89°18'	94°22'	116°24'	87°26'
<i>Oligoclase from Vesuvius.</i>						
0.6322 : 1 : 0.5525	93°28'	116°13'	91°36½'	93°4½'	116°23'	90°4'
<i>Anorthite.</i>						
0.6341 : 1 : 0.5501	94°10'	116°3'	92°34'	93°13'	115°55½'	91°12'

The values of  $A$  and  $B$ , as also those of  $\alpha$  and  $\beta$ , are nearly the same in the three minerals, the chief differences lying in the values of  $C$  and  $\gamma$ . These differences, however are not greater than those exhibited by many other isomorphous substances which are capable of crystallising together. It must be observed also that the magnitudes of the angles, and therefore also the ratios of the axes, are not constant, even for one and the same crystal, but vary with the temperature, and that bodies are comparable with one another, as regards their physical properties, not at the same temperatures, but at temperatures equally distant from their melting points, which differ greatly for the different feldspars. When a triclinic crystal is heated, not only the angles of the faces, but likewise their parametric relations, are altered, as also the angles of the axial planes and of the axes. If the angle of the axes  $a, b$  in oligoclase, which is nearly 90°, is altered in either direction by heating, it will be altered in the opposite manner on cooling, the angle in question becoming in the one case more acute, and causing the

form of the crystal to approximate to that of albite, while in the other case it will become more obtuse, and nearer to that of anorthite.

Lastly, the mode of formation of its twin crystals shows that oligoclase is intermediate between albite and anorthite. In anorthite the axis of combination is parallel to the macrodiagonal; in albite it is perpendicular to the brachydiagonal, while in oligoclase it is sometimes in the first direction, sometimes in the second.

This view of the constitution of triclinic feldspar is further supported by the crystallographic description and chemical analysis of nine of these minerals from different localities lately published by G. vom Rath (*Pogg. Ann.* cxliv. 219).

a. *Andesin* from *Vesuvius*: identical in crystalline form with the formerly-described oligoclase from the same locality.

b. *Oligoclase* from *Niedermendig*.

c. *Oligoclase* from a tourmalin rock in the Veldin, from a coarse-grained mixture of black tourmalin and quartz. The oligoclase appears in crystalline grains an inch in diameter, having a bluish-white colour and a fine, distinct striation on the face P.

d. *Andesin* from the hornblende-melaphyre of Monte Mulatto, near Predazzo: very distinctly striated on *oP*.

e. *Andesin* from the diorite porphyry of Fréjus (Dep. du Var).

f. *Labradorite* from the diorite of the Veldin: a coarse-grained mixture of distinctly striated plagioclase and blackish-green hornblende. The labradorite is bluish-white, and translucent when fresh; snow-white when somewhat decomposed.

g. *Labradorite* from the porphyrite of the Tannbergthal (near Schöneck in the Saxon Voigtland). Nearly transparent and colourless crystals, sometimes 3 centim. long, accompanied by red orthoclase, roundish red quartz-grains, and iron pyrites.

h. *Labradorite* from the dolerite of Hafnefjord in Iceland. This mineral, together with augite, constitutes a doleritic lava, the so-called Klöflava of Iceland, was called *Hafnefjordite* by Forchhammer, who regarded it as a distinct species: but his analysis, which gave 61.2 p.c. silica to 8.8 p.c. lime, appears to have been made on an impure specimen.

i. *Plagioclase* (oligoclase) from the basalt of the Hartenberg in the Siebengebirge. This feldspar which contains a much larger proportion of potash than any of the preceding, may be regarded either as a mixture of albite (8 mol.), anorthite (3 mol.), and orthoclase (3 mol.), or of 3 mol. of an albite rich in potash and 1 mol. anorthite.

The following table contains the results of the analyses of the nine sodio-calcic feldspars above specified. The small figures denote the percentages of silica, &c., as calculated from the formulae:—

*Composition of Sodio-calcic Feldspars.*

	Specific gravity	Silica	Alumina	Lime	Potash	Soda	Magnesia	Ferrio oxide	Total	Ratio of molecules of Albite : Anorthite	Formula
a	2.647	58.53 58.48	26.55 26.49	6.43 8.02	0.89	7.74 7.01	—	—	100.14	4 5	$\text{Na}^8\text{Ca}^1\text{Al}^{11}\text{Si}^{10}\text{O}^{34}$
b	2.611	63.06 63.23	23.27 23.22	4.16 4.22	0.62	8.93 9.33	—	—	100.03	2 1	$\text{Na}^4\text{Ca}^1\text{Al}^{11}\text{Si}^{10}\text{O}^{30}$
c	2.632	61.58 61.12	23.08 22.62	3.49 3.52	0.62	8.98 9.74	—	—	100.65	5 2	$\text{Na}^{10}\text{Ca}^2\text{Al}^{11}\text{Si}^{10}\text{O}^{38}$
d	2.663	60.35 59.73	25.45 25.59	5.14 6.97	1.21	7.63 7.71	0.03	—	99.81	1 1	$\text{Na}^2\text{Ca}^1\text{Al}^{11}\text{Si}^{10}\text{O}^{34}$
e	2.636	58.03 58.48	26.04 26.49	8.07 8.02	0.97	6.16 7.01	—	—	99.87	4 5	$\text{Na}^8\text{Ca}^1\text{Al}^{11}\text{Si}^{10}\text{O}^{34}$
f	2.690	55.25 55.43	29.15 28.49	9.90 10.35	0.80	5.23 5.73	—	—	100.23	1 2	$\text{Na}^2\text{Ca}^2\text{Al}^{11}\text{Si}^{10}\text{O}^{32}$
g	2.711	53.61 54.02	22.68 29.45	10.96 11.46	1.15	4.36 5.07	—	—	99.76	2 5	$\text{Na}^4\text{Ca}^2\text{Al}^{11}\text{Si}^{10}\text{O}^{32}$
h	2.729	54.23 54.02	29.64 29.45	12.01 11.46	trace	4.41 5.07	0.11	—	100.40	2 5	$\text{Na}^4\text{Ca}^2\text{Al}^{11}\text{Si}^{10}\text{O}^{32}$
i	2.632	63.56 63.93	21.81 21.90	2.32 2.98	3.65	6.84 7.45	0.95	0.66	99.81	3 1	$\text{K}^1\text{Na}^4\text{Ca}^2\text{Al}^{11}\text{Si}^{10}\text{O}^{32}$



The composite nature of these feldspars is indicated by the striation of some of their faces, which would naturally result from the juxtaposition of a number of thin lamellae of two different minerals.

Two sodio-calcic feldspars from the Ural, analysed by vom Rath (*Pogg. Ann.* cxlvii. 274), exhibit a similar constitution :—

a. Oligoclase from Scheitansk near Mursinsk, where it occurs in clefts in the granite which formerly yielded the well-known red tourmalines. The crystal examined measured 3 or 4 centimeters in its several dimensions; it is terminated at both ends by the cleavage-faces *oP*. It is transparent and colourless, which is seldom the case with sodio-calcic feldspars, and is more like adularia and some varieties of sanidine, in not exhibiting the twin-striation parallel to the brachydiagonal which is usually seen in triclinic feldspars. Sp. gr. 2.642 (at 18°). Loss by ignition 0.38 :—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	CaO	MgO	K <sup>a</sup> O	Na <sup>a</sup> O
63.83	22.58	3.42	0.06	1.02	8.86 = 99.77

Oxygen ratio: (CaO + K<sup>a</sup>O, Na<sup>a</sup>O) : Al<sup>a</sup>O<sup>a</sup> : SiO<sup>a</sup> = 0.985 : 3 : 9.687. In composition this mineral is more nearly related to the oligoclase from the tourmaline-rock of the Veltin than to any other of the nine triclinic feldspars, and, like the latter, may be regarded as a mixture of 5 parts by weight of albite and 1 part of anorthite.

b. Andesin from the Uvelka mountain near Orenburg : a fragment 7 centimeters long and broad, 2½ centimeters thick, marked on the very perfect cleavage-face *oP*, with an extremely fine striation, which, however, does not cover the whole face. The mineral is fresh, translucent, white, reddish in some parts from admixture of a small quantity of iron-glance. The feldspar is intergrown with grey quartz and black mica, the latter being sometimes interlaminated in a peculiar manner parallel to *oP*. Sp. gr. 2.651. Loss by ignition 0.33 :—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	CaO	K <sup>a</sup> O	Na <sup>a</sup> O
60.34	24.39	0.18	5.56	0.73	8.44 = 99.64.

Deducting the ferric oxide, which probably belongs to the iron-glance, the oxygen-ratio is 1.025 : 1 : 8.478.

This andesin is most nearly related to that from the melaphyre of Monte Mulatto near Predazzo (p. 512), and, like the latter, cannot be exactly represented in composition by a mixture of albite and anorthite. If we start from the proportion of lime and alkalis shown by the analysis, the proportion of silica comes out rather too high for such a mixture; and if, on the other hand, we start from the observed quantity of silica, the calculated quantity of the lime is too great in proportion to that of the soda.

Rammelsberg has lately pointed out that the analysis of every sodio-calcic feldspar yields two atomic ratios, namely, that of Al<sup>3</sup> : Si and that of Na : Ca. He designates as normal analyses those in which these two ratios lead to the same result. It is only however, in about 10 p.c. of the analyses discussed that this condition is exactly fulfilled; in 40 p.c. the two ratios lead to nearly the same proportion of albite and anorthite, while in the remaining 50 p.c. the calculation founded on the ratio Ca : Na leads to a result essentially different from that which is founded on the ratio Al<sup>3</sup> : Si.

The analysis of the Scheitansk feldspar gives Al<sup>3</sup> : Si = 1.484, corresponding with a mixture of 5 mol. albite and 2 vol. anorthite, which requires Ca : Na = 1.5. Now the analysis, after conversion of the potash into its equivalent quantity of soda, gives Ca : Na = 1.502, showing that this mineral has the normal constitution of a sodio-calcic feldspar.

In the Orenburg mineral, Al<sup>3</sup> : Si = 1.425, corresponding with 5 mol. albite + 4 mol. anorthite, which requires Ca : Na = 1.25, whereas the analysis, after conversion of the potash into the equivalent quantity of soda, gives Ca : Na = 1.290. If, on the other hand, we start from this, the ratio Al<sup>3</sup> : Si becomes = 1 : 4.367. The Orenburg mineral belongs, therefore, to those sodio-calcic feldspars in which calculation from the two ratios leads approximately to the same result.

Petersen (*J. pr. Chem.* [2], vi. 197) objects to the mixture theory of the sodio-calcic feldspars, chiefly for the following reasons:—1. The striation peculiar to plagioclase feldspars is not always observed where it might be expected to occur; orthoclase from the syenite of Laurvig in Norway, containing a large amount of soda, does not show it; neither does the plagioclase from the basalt of the Hartenberg in the Siebengebirge, though very rich in potash, exhibit any trace of admixture of orthoclase. 2. Admitting the possible isomorphism of albite and anorthite, it is nevertheless difficult to imagine the replacement of Si<sup>2</sup> by CaAl<sup>3</sup>, or of Ca<sup>2</sup>Al<sup>3</sup> by Na<sup>2</sup>Si<sup>2</sup>, and it appears scarcely necessary to admit special laws of isomorphism in the case of the feldspars, when no such supposition is made in other cases of similar character. A well-defined transparent crystal of calcspar, for example, containing a considerable

proportion of magnesium, is still regarded as calcspar, and not as a mixture of calcspar and bitter spar. Garnet also, though sometimes richer in ferrous or manganous oxide, sometimes in lime or magnesia, nevertheless forms well-defined, transparent, homogeneous crystals, which can scarcely be regarded as mixtures. The same is the case with the hyalophane of Binnenthal, which has the composition  $\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$  ( $\text{R} = \frac{1}{2}\text{Ba} + \frac{1}{2}\text{K}_2\text{Na}^2$ ), and shows that a large proportion of potash renders felspars monoclinic. There are also numerous cases of artificially prepared crystals containing several isomorphous elements, which cannot easily be regarded as mixed crystals. Weltzien's experiments have shown how much copper can be introduced into rhombic zinc sulphate,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ , or into monoclinic ferrous sulphate,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ , without altering the crystalline form or the amount of water. This could scarcely be the case if the crystals containing copper were mixtures. 3. Anorthite is easily and completely decomposed by strong hydrochloric acid, whereas oligoclase is scarcely attacked: hence, according to the mixture theory, hydrochloric acid might be expected to dissolve out the lime-constituent of sodio-calcic felspars more easily than the soda-constituent, but such is not the case. 4. Oligoclase from the diorite of Hof and from the diabases is free from lime; that from the gneiss of Aschaffenburg contains only a trace of lime. In all these oligoclases the oxygen-ratio of the alkalis, the alumina and the silica is as 1 : 3 : 10, whereas in albite and orthoclase it is as 1 : 3 : 12. 5. Although crystals of albite are found intergrown with those of orthoclase and *vice versa*, nevertheless transparent orthoclases rich in soda are perfectly homogeneous, and probably therefore contain soda as an essential constituent. Since, then, these orthoclases rich in soda, and transparent albites rich in potash, must be regarded, not as mixtures, but as individual bodies, the same is most probably the case with oligoclase, labradorite, and andesine, which last Petersen regards as only an oligoclase rich in lime.

*Decomposition of Felspar by Saline Solutions.*—Birker and Ulbricht (*Annalen der Landwirtschaft*, 1871, 170) have examined the influence of saline solutions and other agents on the weathering and decomposition of felspar. For this purpose 1 kilogram of powdered felspar and 2½ litres of distilled water were placed in a flask, together with the substances mentioned below, the amount of dissolved ingredients being determined after the materials had remained together for about 2½ years.

In the cases in which air or carbonic anhydride was used, the gas was passed to the bottom of the flask at intervals of from 2 to 4 weeks; in the other cases the flasks were made air-tight, and shaken at the same intervals.

The felspar used contained 8.51 p.c.  $\text{K}_2\text{O}$ , 3.37  $\text{Na}_2\text{O}$ , 1.3  $\text{BaO}$ , 16.03  $\text{Al}_2\text{O}_3$ , and 65.52  $\text{SiO}_2$ .

In the following table the quantities of ingredients found in solution are given in grams:—

Experiments	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{SO}_3$	$\text{SiO}_2$
1. Distilled water . . . . .	.051	.078	.058	.006	.044	.049
2. Ditto, with air . . . . .	.037	.064	.044	.005	.044	?
3. Ditto, with $\text{CO}_2$ . . . . .	.071	.114	.076	.004	.046	.069
4. Caustic lime . . . . .	.209	.174	.067	.003	.041	.061
5. Calcium carbonate . . . . .	.042	.073	.112	.009	.040	.019
6. Ditto, with $\text{CO}_2$ . . . . .	.067	.094	.273	.018	.041	.034
7. Calcium sulphate . . . . .	.053	.074	1.906	.016	2.840	.033
8. Ditto, with $\text{CO}_2$ . . . . .	.068	.097	1.958	.016	2.684	.062
9. Calcium nitrate . . . . .	.041	.062	—	.016	.048	.036
10. Ditto, with $\text{CO}_2$ . . . . .	?	—	—	.017	.048	.045
11. Ammonium sulphate . . . . .	.161	.094	.122	.035	—	.066
12. Ditto, with $\text{CO}_2$ . . . . .	.162	.107	.147	.015	—	.056
13. Magnesia . . . . .	.359	.315	.013	.004	.065	.169
14. Ditto, with $\text{CO}_2$ . . . . .	.312	.255	trace	—	.111	.048
15. Potassium carbonate . . . . .	—	—	trace	trace	.048	.026
16. Ditto, with $\text{CO}_2$ . . . . .	—	—	.029	.007	.040	.029
17. Sodium nitrate . . . . .	.080	—	.049	.003	.043	.060
18. Ditto, with $\text{CO}_2$ . . . . .	.096	—	.120	.008	.037	.032
19. Sodium chloride . . . . .	.163	—	.091	.008	.040	.032
20. Ditto, with $\text{CO}_2$ . . . . .	.183	—	.123	.006	.034	.057
21. Ferrous hydrate, with air . . . . .	.086	.069	.040	.004	.052	.036

From these numbers it is seen that the action of distilled water with and without air was practically the same. Calcium carbonate, calcium nitrate, with and without carbonic acid, gypsum with and without carbonic acid, potassium carbonate and bicarbonate, and ferrous hydrate, had little more action than water alone. Carbonic acid, and calcium carbonate with carbonic acid, showed an increased action on the alkalis and silica. In the experiments with lime a much larger quantity of alkalis was dissolved, the lime at the same time entering into combination with the silica. Sulphate of ammonia had an energetic action, more especially on the potash; only in the experiments with this salt and in that with lime, was potash dissolved in larger quantity than soda. In the case of the ammonia sulphate, the base had entered into some combination with the silica, which was not decomposed either by washing until all sulphuric acid was removed, or by heating to 100° C. Eichhorn (*Jahresb. f. Agrikulturchemie*, 1859-60, 16) has already shown that silicates which are decomposed by hydrochloric acid, such as chabasite, absorb ammonia from its salts. Magnesia acted more energetically than any other agent, seven times more alkalis and three times more silica being dissolved with its aid than with water alone. Its somewhat slower action in combination with carbonic acid was probably due to the crystallising of bicarbonate on the sides of the vessel.

Sodium nitrate dissolved about double the quantity of potash that water did, but its action was less than that of sodium chloride. These comparative results are in unison with those of Dietrich on basalt (*J. pr. Chem.*, lxxiv. 12, and *Jahresb. f. Agrikulturchemie*, 1862-63, 14).

**FERMENTATION.** Liebig (*Ann. Ch. Pharm.* cliii. 137) has continued his experiments with reference to Pasteur's germ-theory of Fermentation (*1st. Suppl.* 612). Pasteur regards the formation of acetic acid from alcohol in the ordinary process of vinegar-making, as essentially dependent on the presence of a peculiar fungus, the *Mycoderma aceti*. According to Liebig, on the other hand, it is a simple process of oxidation. Many organic substances possess, as observed by Schönbein, the power of absorbing oxygen from the air, just like finely divided platinum, the oxygen thus taken up being transferable to other bodies and capable of oxidising them. This indeed was shown thirty years ago by De Saussure, who oxidised hydrogen by contact with organic matters in a state of putrefaction or decay. In the same manner vapour of alcohol is oxidised in contact with decaying wood, the latter being used, as is well known, in the quick method of vinegar-making. A wood-shaving which had been used in a vinegar-work for twenty-five years, did not exhibit, on microscopic examination, the slightest trace of a fungus. Mother of vinegar may in like manner bring about the oxidation of alcohol, but the process is not a physiological one, and the acetic acid is a product, not of a fungus, but of oxidation.

The processes of decomposition of organic matters may be divided into three groups, the first including alcoholic, lactic and butyric fermentation; the second and third, the formation of acetic and of nitric acid, and the fermentation of urino. Fermentations of the first class, when once set up, do not require the further aid of oxygen, whereas in those of the second and third class, oxygen plays a definite part. Urinary fermentation is determined by the two processes going on simultaneously, and the same is true with regard to the putrefaction of animal bodies and to the fermentation of dextrin in beer-wort.

Pasteur on the other hand (*Compt. rend.* lxxiii. 1419) defends his views on alcoholic and acetic fermentation, and maintains the exactness of the experiments on which they are based. He states that he has been able to produce fermenting media by bringing together only three kinds of substance, namely a fermentable body, properly selected mineral salts, and fermentative germs. If, for example, to a very pure solution of crystallised calcium lactate there be added the phosphates of ammonium, magnesium, and calcium, together with small quantities of ammonium sulphate, and finally vibrios or fully developed vibrios, the lactate will disappear in a few days, and an immense number of new vibrios will be developed. As long as any calcium lactate remains, the vibrios multiply and move about in the liquid; but when the whole of the lactate is decomposed, the vibrios fall dead to the bottom. Moreover not the smallest quantity of wine ever turns sour in contact with the air, without the previous presence of *Mycoderma aceti*.

Pasteur moreover finds (*Compt. rend.* lxxv. 784) that if a saccharine liquid suitable for fermentation be put in a vessel in which it can be sown with a particular organism, without fear of any other getting into it spontaneously from the air, and then a trace of pure *Mycoderma vini* be sown in it, the liquid will in a few days be completely covered with a pellicle of the fungus, which can be shown to grow at the expense of the air, absorbing its oxygen, and giving out nearly the same volume of carbon dioxide, and to produce no alcohol in the liquid. If now the pellicle be submerged in the liquid,

bubbles of carbon dioxide soon begin to rise from it, and alcohol is formed; at the same time its cells swell up and cease to multiply, and the internal structure of their plasma becomes very greatly modified. Thus the same cells acquire or lose the power of acting as a ferment, according as they are deprived of air, or exposed to it. This experiment also succeeds with the true fungi, such as *Penicillium glaucum*.

Yeast and other ferments therefore differ from the other lower organisms only in possessing the faculty of living and multiplying regularly and continuously without contact with the atmosphere. These observations appear to remove the mystery of fermentation. Instead of requiring free oxygen to burn the materials which serve for their nutrition, they obtain the heat necessary to their existence by living upon oxygenated bodies like sugar, which can furnish heat by their decomposition.

Viewing fermentation in this light, all living bodies may become ferments under certain conditions. Thus, when an animal is suddenly killed, life does not at once cease in the organs of the body, or in the physiological elements of these organs, and when this goes on in them without the influence of free oxygen, it does so at the expense of the surrounding materials from which the necessary heat is obtained, and they behave like ferments to these materials.

Bérard has shown that when fruits are exposed to the air, they absorb oxygen and replace it by carbon dioxide, but that when placed in an inert gas, like carbon dioxide itself, they also evolve carbon dioxide. The gas evolved under the latter circumstances he considers to be a product of a sort of fermentation. Pasteur confirms this view, for he finds that alcohol is formed even when the fruit is placed in an inert gas. When this experiment is made with suitable precautions, no beer-yeast or other ferment is produced.

Grapes thus exposed to carbon dioxide acquire at the same time exactly the odour and flavour of expressed grape-juice, quite distinct from that of the fresh grape.

Dumas (*Compt. rend.* lxxv. 277) regards fermentation as the chemical decomposition of sugar by the vital force of yeast-cells, and considers that Pasteur's researches have placed the matter beyond dispute. He has himself made a number of experiments, the results of which are opposed to the views of Berzelius and of Liebig, and show that fermentation is not merely set going by the ferment, but is continuously dependent upon it, and susceptible of measurement and modification like any other chemical phenomenon.

In one series of experiments he endeavoured to transmit the movements of a fermenting solution of sugar to a solution of pure sugar separated from it either by various liquids or by a septum of collodion, or else resting upon it in direct contact, and failed in every case to do so, or even to cause the inversion of the sugar.

Berzelius having attributed the fermentation of sugar to the contact-action of the yeast, Dumas tried the effect upon sugar of another chemical phenomenon also attributed to contact, namely, the liberation of oxygen from hydrogen dioxide and manganese dioxide. This was effected in a solution of sugar, and produced no change whatever in it. Various other chemical actions excited in a solution of sugar were also found to be without any effect upon it; so that its alcoholic decomposition cannot apparently be produced by another chemical action.

Schönbein has shown that ozone and hydrogen dioxide are formed during slow combustions, and among these Liebig classes fermentations; but Dumas does not find that either ozone or hydrogen dioxide is produced during fermentation. Oxygen passed through a fermenting liquid does not appear to affect it in any way.

By dividing a mixture of yeast and water equally among solutions of sugar, the yeast being always in excess, it was found that, under similar circumstances as regards pressure and temperature, the duration of the fermentation was proportional to the quantity of sugar. Cane-sugar requires twice as long for its fermentation as glucose; so that as much time is required to invert the sugar as to ferment it. It is estimated that about 400 milliards of yeast-cells are required to ferment a solution of one gram of pure cane-sugar in one hour. Fermentation proceeds more slowly in darkness, and in a vacuum.

Neutral gases do not affect the power of yeast. Sulphur, in a fermenting liquid, is converted into hydrogen sulphide having an odour of onions, and appears to be the only substance, besides sulphuretted compounds, that enters into reaction with ferments. Yeast is by this reaction shown to be a reducing agent. Sulphur does not appear to hinder fermentation, as it has been stated to do. Very dilute acids do not affect fermentation: larger doses destroy it. Very dilute alkalis retard fermentation: larger doses arrest it. Alkaline carbonates hinder it only in very large doses.

Sal ammoniac causes yeast to precipitate almost as rapidly as potato-starch deposits from water. Potassium silicate and borax conglutinate it, so that it becomes clotted like silver chloride.

When fresh yeast is placed in a saturated solution of *neutral potassium tartrate*, no change is perceived, and on removing the yeast to a solution of sugar, fermentation almost instantly commences, and rapidly follows its course. But the liquid, after the fermentation, presents all the characters of a solution of ordinary albumin. When the tartrate, the yeast, and the sugar and water are mixed together at once, no such effect is produced; so that it must be caused in the other case, 1st, by the absorption of the saline solution by the yeast, and 2ndly, by the displacement of this by the sugar solution. The action of the neutral tartrate and of such salts as potassium silicate, borax, soap, &c., can therefore effect a physiological analysis of yeast, similar to that of blood by the action of certain neutral salts.

The *acid tartrate of potassium* and some other salts seem rather to favour fermentation; others retard it; others, again, such as *common salt*, permit inversion of the sugar to occur, but prevent its fermentation, while others altogether prevent both inversion and fermentation, these being potassium cyanide, potassium monosulphide, and strange to say, potassium acetate.

*Sodium sulphite* and *thiosulphate*, and *potassium sulphocyanate* furnish, by a fermentation which sometimes soon ceases, and sometimes continues to its natural termination, an alcoholic liquid which, when distilled with solution of potash, yields an alcohol containing aldehyde and a matter exhaling a very agreeable fruity odour. The alcohol becomes milky when mixed with water. The potash-solution deposits much aldehyde-resin on cooling, and yields on evaporation salts having special characters.

*Potassium thiosulphate* disengages hydrogen sulphide during the whole of the fermentation, and the product which accompanies the alcohol exhales an odour of garlic.

Lastly, with regard to the action of salts as bearing upon the theory of fermentation, it may be mentioned that when, as in the presence of the acid potassium tartrate, fermentation proceeds actively, the yeast-cells are clear, well defined, and full of a plastic matter containing brilliant and very active corpuscles, and send out numerous offshoots; whereas, when the fermentation languishes, as in the presence of salts of iron or manganese, the cells appear contracted, tuberculated, granular, and shrivelled, and, without recent offshoots.

A solution of *borax* conglutinates yeast, and the supernatant liquid cannot, like yeast-water, invert cane-sugar. Borax prevents the action of yeast-water upon sugar, of *emphase* upon amygdalin, also that of *diastase* upon starch, and the action of *myrosin*. (Dumas.)

According to Béchamp (*Compt. rend.* lxxv. 1036), two yeasts, apparently identical and pure, do not always yield the same results. Under the same conditions, yeast from the same lot always produces an equal quantity of acetic acid; but, other things being equal, one sample of yeast may produce four times as much acid, or may require a time four or five times as long to complete the fermentation, as another. Contact with the air, even with a large surface, far from augmenting the quantity of acetic acid, diminishes it, but generally shortens the period required for the fermentation.

In experiments made in apparatus where the air was displaced by a current of carbonic anhydride, from two to four times as much acetic acid was produced as in similar experiments made under exposure to the air. It is possible to produce in a saccharine solution a weight of acetic acid greater than the dry weight of the yeast used; the acid cannot therefore come from the yeast. The hotter the yeast is nourished in the solution, the less is the amount of acid produced. An increase of temperature shortens the duration of the fermentation, and augments the amount of acid. Pressure increases the quantity of acid.

*Influence of Pressure on Fermentation.*—Experiments on this subject have been made by H. T. Brown (*Chem. Soc. J.* [2], x. 570; xi. 973). He finds that during the alcoholic fermentation of grape-juice or malt-wort, besides carbonic anhydride, there are evolved—nitrogen, hydrogen, and hydrocarbons of the paraffin group, and sometimes nitric oxide; that, moreover, the proportion of the gases unabsorbed by potassium hydrate is largely increased when the operation is carried on under diminished pressure. At the ordinary pressure, by far the larger proportion of these gases is nitrogen (70 to 90 p.c.), but under diminished pressure (400 to 450 mm.), the hydrogen preponderates (60 to 90 p.c.) Nitrogen, however, does not occur when the solutions are free from albuminoids, even if ammonium salts are present in considerable quantity. The increase of the proportion of hydrogen, resulting from diminution of the pressure, is accompanied by formation of a comparatively large amount of acetic acid and aldehyde, so that it would seem that water is decomposed during the alcoholic fermentation, and that this result is facilitated by the diminution of the pressure. The presence of nitric oxide in the evolved gases was found to be due to the reduction of nitrates originally present in the solutions.

Diminished pressure retards the progress of the alcoholic fermentation in a remarkable way, although there does not seem to be any simple relation between them. It is certain, however, that under diminished pressure less sugar is decomposed than during an equal time at the ordinary pressure, and that the proportion of the carbonic anhydride to the alcohol produced is greater. This difference is not due to any injury of the yeast cells caused by the removal of the pressure, but appears rather to be an exemplification of Morby's law, 'that pressure weakens or strengthens chemical affinity, according as it acts against or in favour of the change of volume;' there is indeed a decided contraction in volume during the alcoholic fermentation. The acetic acid produced is derived directly from the sugar.

*Influence of Temperature.*—According to J. Pierre (*Compt. rend.* lxxiii. 317), the more rapid fermentation of sugar which takes place at comparatively high temperatures is attended with a more abundant formation of the higher alcohols, butylic and amylie, and consequently with a diminished production of ethylic alcohol. When the temperature is kept down to the lowest point at which fermentation can go on, scarcely any butylic or amylie alcohol is obtained, but propylic alcohol is formed, which, in testing by the alcoholimetric process, is reckoned as common alcohol.

*Alcoholic Fermentation by means of Mucor Mucedo.* (A. Fitz, *Dent. Chem. Ges. Ber.* vi. 48–58).—De Bary in 1857, and afterwards Rees, discovered that the mould-fungus, *Mucor Mucedo*, immersed in saccharine solutions, is capable of setting up the alcoholic fermentation, the spores of the fungus multiplying by gemmation after the manner of beer-yeast. The mucor cells, however, are easily distinguished from yeast cells by their enormous size and by the red coloration produced by zinc chloride in their cellulose envelope. In the presence of air, mucor also develops a luxuriant mycelium. Fitz also finds that the spores of this fungus develop differently according to the presence or absence of oxygen. In the absence of oxygen, they multiply by gemmation, and alcoholic fermentation is set up, but in the presence of air, a luxuriant reticulated mass is produced, no fermentation occurring at first, but only oxidation of the sugar through the agency of the mycelium. This continues till the oxygen is consumed, when the mycelium breaks up into isolated cells, and fermentation commences.

Mucor fermentation proceeds best at a temperature between 25° and 28°. The gas evolved is pure carbonic anhydride.

Mucor yeast is very sensitive to the presence of alcohol, and the fermentation soon comes to an end. Mucor can only be employed for the fermentation of solutions containing less than 7 per cent. of sugar, and is therefore useless for the fermentation of wine.

Succinic acid is formed in the mucor fermentation, but no glycerin has been detected in the product of the reaction.

Dextrin, inulin, and milk-sugar do not ferment under the influence of mucor.

*Alcoholic Fermentation of Milk-sugar.*—Blondlot finds that milk, under favourable circumstances, produces a special alcoholic ferment, which differs from ordinary yeast in requiring agitation to enable it to become active, in operating in an intermittent manner, requiring rest and agitation alternately, and in not manifesting any action below 20°. A temperature of 30° to 35° is the best for the purpose. No carbonic acid gas is evolved until the milk is shaken, and the quantity diminishes gradually as the fermentation approaches completion. When the fermentation has ceased, an addition of milk-sugar or of ordinary glucose causes it again to become active. The alcohol produced has an agreeable taste, but is apparently contaminated with a little butylic alcohol.

*New Theory of Alcoholic Fermentation.*—A. Petit (*Compt. rend.* lxxiii. 267) supposes that in a solution of sugar containing globules of yeast, water is decomposed, the oxygen uniting, at least for a moment, with the substance of the globules, while the hydrogen in the nascent state attaches itself to a molecule of sugar, and causes its decomposition, the products being alcohol, carbonic anhydride, and one molecule of hydrogen, which decomposes a further molecule of sugar, and so the reaction proceeds:—



A single molecule of hydrogen should therefore theoretically decompose an indefinite quantity of sugar, were it not that secondary reactions occur, the principal of which consists in the formation of glycerin:—



The reason for considering the hydrogen the primo agent—although the oxygen might equally well be so regarded, and nothing proves that under certain conditions of ex-

periment it is not so—is that, on allowing two similar liquids to ferment, but with the addition of 1 p.c. of sodium sulphite to the one, the same disengagement of carbonic anhydride took place in both cases, although the oxygen had served to convert the sulphite into sulphate. In this experiment no acids were formed.

If the fermentation takes place in the absence of sulphites, the oxygen forms succinic and acetic acids.

**Fermentation of Fruit.**—Fruit protected from the air evolves considerable quantities of carbon dioxide, alcohol and acetic acid being at the same time formed in the interior, whilst a proportionate diminution takes place in the quantity of sugar contained in the fruit.

(Observations on the fermentation of apples yielded the results given in the following table:—

	Duration of expt.	Weight of apples	Loss of weight	Loss of sugar	Gas evolved	Alcohol	Acetic acid
	hours	grams	grams	grams	grams	grams	grams
1 . . .	184	348.0	14.3	26.0	13.10	10.01	0.11
2 . . .	157	353.6	7.6	6.0	5.30	4.00	0.10
3 . . .	234	531.5	22.5	36.4	21.05	20.56	0.29
4 . . .	150	407.3	31.3	45.6	24.50	21.80	0.35
5 . . .	124	338.9	3.9	5.4	3.00	2.89	0.17
6 . . .	184	341.0	4.0	—	2.40	4.27	0.17

In the later stages of the evolution of carbon dioxide, the alcoholic ferment was invariably found to be fully developed, and budding at all parts of the interior of apples, the peel of which remained intact. In the juice of apples the globules became transformed into long chains in the course of a few hours. During the first stage of evolution of gas, however, no ferment in the growing state was found either in the apples or in the juice expressed from them. The juice contained only isolated globules of various sizes: but even at this stage, alcohol was formed, as shown by experiment 5.

The ferment in the budding state was not observed in apples exposed to the air. The question, whether in this case alcohol is formed in the fruit, is not yet decided.

The gas evolved from the interior of an apple under reduced pressure was found to contain 15 p.c. of oxygen and 5 of carbon dioxide, the rest being nitrogen. The gas evolved from mellow or rotten apples contains no oxygen (Lechartier a. Bellamy, *J. Pharm.* [4], xiii. 251; *Compt. rend.* lxxv. 1203).

The following observations on the fermentation of bilberries, wine, and honey have been made by Boussingault (*Ann. Ch. Phys.* [4], xxvi. 362).

*Bilberries* (fruit of *Vaccinium Myrtillus*).—The berries were allowed to ferment spontaneously in a flask connected with a jar standing over mercury.

Bilberries	Weight employed	Containing		Acid expressed as H <sup>2</sup> SO <sup>4</sup>
		Sugar	Alcohol	
Before fermentation . .	grams 9486.5	grams 598.6	grams 0.0	grams 64.32
After . . . . .	0166.3	0.0	239.63	64.88
Difference . . . . .	—320.2	—598.6	+239.63	+0.56

The sugar, which, judging by its rotatory power, seemed to be wholly inverted sugar, should have given 305.9 of alcohol; only 239.63, or 78 per cent. of this was obtained.

These 239.63 grams of alcohol produced represent 229.3 grams of carbonic anhydride. The loss of weight after fermentation was 320.2, and there was, as shown in the table, but very inconsiderable increase in the proportion of acid.

*White Wine of Lampertloch*.—Must of sp. gr. 10795 at 17° was taken and strained from the stalks, skins, and stones.

## FERMENTATION.

*Fermentation of White Wine.*

	Weight of must	Sugar by copper test	Alcohol	Acid expressed as H <sup>2</sup> SO <sup>4</sup>
Before fermentation	grams 9715.5	grams 1688.46	grams 0.0	grams 30.74
After            ,,	8955.0	traces	781.41	47.82
Difference	-760.5	-1688.46	+781.41	+8.08

The alcohol obtained was about 91 p.c. of the amount which the sugar should theoretically have yielded.

The alcohol produced represents 747.8 of carbonic anhydride, the loss actually experienced being 760.5.

By a series of observations of the rotatory power of the must during the progress of the fermentation, it was found, as already shown by Dubrunfaut, that the dextro-glucose is destroyed by fermentation before the levulose.

*Honey.*—Fermented with washed beer yeast.

	Volume	Weight	Sugar by copper test	Alcohol	Acid expressed as H <sup>2</sup> SO <sup>4</sup>
Before fermentation	litres 3.845	grams 4012.87	grams 378.73	grams —	grams 0.62
After            ,,	3.837	3823.00	traces	177.65	3.07
Difference	-0.008	-189.87	-378.73	+177.65	+2.45

The sugar should have produced 193.57 grams of alcohol. Calculating from the alcohol produced, 170 grams of carbonic anhydride should have been evolved. The actual loss incurred was nearly 190 grams.

**Nature and Origin of Ferments.**—A. Mayer (*Ann. Chem. Pharm.* clvii. 227) has made a series of experiments on alcoholic fermentation and the mode of nutrition of the yeast-plant, from which the following conclusions are drawn. The salt most intimately related to the proper physiological function of yeast—the conversion of sugar into alcohol and carbon dioxide—is acid potassium phosphate, since the exclusion of that salt exerts immediately, and directly, an injurious effect upon the fermentative process. It cannot be replaced by the sodium or ammonium phosphates, or by any other salt of potassium.

Other salts are, however, necessary to the complete nutrition of the yeast-plant. If a mixture of water, sugar, and an appropriate nitrogenous body, in proper proportions, be taken, and no mineral constituent except potassium phosphate be added, fermentation sets in actively, after the addition of a very small quantity of yeast, but after a time the yeast-cells are found to be incompletely formed, and they are no longer capable of keeping up vigorous alcoholic fermentation.

The salts which prevent this degeneration of the yeast-plant, and so must be regarded as food for it, are those of magnesium, although these stand in no direct relation to the decomposition of the sugar. The minutest quantity of sulphur suffices for the nutrition of the yeast-plant, and this substance appears to be present even in the purest sugar-candy. All the other constituents of the ashes of the plant bear no relation to its nutrition, and calcium may be entirely removed without injury.

These results show that the requirements of the yeast-plant are much simpler than those of the higher plants and animals. Iron, for instance, and probably calcium may be completely absent from growing yeast. It is also manifest that the several functions of plants demand specific forms of nutriment for their due performance.

With regard to the nutrition of yeast by nitrogenous substances, the following results were obtained: they are somewhat different from those commonly received. The albuminous, and many other highly organised bodies, are ill adapted to the nutrition of the yeast-plant. Ammonium salts, and nitrogenous organic substances similar in constitution to ammonia, are quite competent to the nutrition of the yeast-plant. But this plant differs from the higher vegetable organisms in being incapable of de-



giving the chief portion of its nitrogen from the nitrates. Pepsin was found to be the best food for yeast, and the diastase of beer was also found to be a good nitrogenous substance for this purpose, and for supporting vigorous alcoholic fermentation; but with respect to diastase, it was found that this result in no way depended upon the facility with which that body ferments, for previous heating of the liquid to the boiling point exercised no influence on the subsequent fermentation by means of yeast.

During alcoholic fermentation yeast not only decomposes sugar into alcohol and carbon dioxide, but the organism secretes unknown nitrogenous substances which are no longer capable of affording nourishment to the plant.

With regard to the connection between the nutrition of the yeast-plant and alcoholic fermentation, Mayer's experiments show that yeast does not require the access of free oxygen for its growth, and differs in this respect from other vegetable organisms; it does not *breathe* in the same sense as the higher plants, animals, and even other fungi do. The dictum that every organism, in order to furnish manifestations of life, must appropriate oxygen, cannot, therefore, be unreservedly admitted, and the following is proposed as a substitute for it:—that for the completion of the manifestations of vitality in every organism, chemical forces must come into play, such chemical forces being transmuted into heat and mechanical motion; further, that the chemical forces derived from the affinity for oxygen of organic substances in plants must be considered only as a special case of the above general law, although the most common one. If this modification of the generally received theory be admitted, the vital changes undergone by yeast in a saccharine solution may be classed with those changes of matter which take place in the higher organisms, and at the same time the series of phenomena taking place during the growth of the yeast-plant become explicable. The splitting up of a carbo-hydrate into alcohol and carbon dioxide is accompanied by a loss of chemical force—the alcohol formed having a much smaller thermic equivalent than the sugar from which the alcohol was formed. The case is one of internal combustion (*innere Verbrennung*). Moreover, the formation of cellulose in the cell-wall of the newly formed yeast-plant is a case of splitting up of sugar into more highly and less oxidised products, and during the process there is a consumption of chemical force. The connection between the splitting up of the sugar and the budding of the yeast-plant is thus indicated with much probability.

From the experiments of Béchamp (*Compt. rend.* lxxviii. 877) it appears that, under some circumstances, the mother of vinegar, a conglomeration of microzymes, can be transformed into bacteria, and under other circumstances into a cellular ferment which can produce the normal alcoholic fermentation from cane-sugar. Subsequent researches (*Ann. Ch. Phys.* [4], xliii. 443) have shown that the converse of this is also true, and that the cellular ferment may be transformed into microzymes and bacteria.

A mixture of starch and yeast kept at a temperature of  $24^{\circ}$ – $35^{\circ}$  soon liquefies, and the yeast undergoes remarkable changes. The cells swell, become transparent, and gradually disappear. Myriads of microzymes of great agility spring into existence, then vibrios appear, and as these increase the microzymes diminish. The vibrios in their turn are succeeded by myriads of bacteria, and finally the bacteria gradually disappear, leaving nothing present but microzymes, simple or coupled together. During these changes a small quantity of gas is disengaged; no butyric acid is formed, and but little acetic and lactic acids.

A similar experiment made in presence of calcium carbonate produces somewhat similar physiological results, but, in addition, the vibrios are preceded or accompanied by a crowd of little bodies resembling the *amylobacters* of Trécul (*Compt. rend.* lxxiii. 1153), which, however, soon disappear, leaving only bacteria present. In this experiment pure carbon dioxide is disengaged at first, and afterwards a mixture of carbon dioxide and hydrogen. The soluble starch and dextrin disappear, producing a corresponding quantity of alcohol, acetic, and butyric acids. The ferments which proceed from these operations can serve indifferently as lactic or butyric ferment.

As, then, the mother of vinegar when changed into bacteria becomes lactic or butyric ferment, and when transformed into cellular matter becomes alcoholic ferment, and as pure yeast becomes lactic or butyric ferment when reduced to microzymes, vibrios, or bacteria, it is evident that the property of being a ferment of any particular nature does not depend essentially upon the matter of the ferment, but upon its organisation or structure.

Liebig contested the statement that an alcoholic ferment can be produced in a saccharine mixture without the previous addition of an albuminoid substance. Béchamp, however (*Compt. rend.* lxxiv. 125), arrives at a contrary conclusion. A mixture of 250 grams of cane-sugar, 1 gram of magnesium phosphate, 0.5 gram of calcium phosphate, and 1,500 c.c. of water, when exposed to the air, soon becomes very acid; gas is given off as abundantly as in a fermentation with ordinary yeast; and in 91 days, when the evolution of gas has ceased, the mixture yields 356 c.c. alcohol of  $86^{\circ}$ .

Acetic acid is also present, but neither butyric nor lactic acid. The ferment consists of very small oval cells and mobile granulations. Experiments with cane-sugar and other salts, as potassium nitrate, sodium phosphate, alum, &c., gave very similar results.

Béchamp also finds that beer-yeast, when suspended in water, exhausts itself and secretes phosphoric acid, and that amongst other products formed, one, named by him *zymase*, is capable of inverting cane-sugar. The phosphoric acid and *zymase* exist in the interior of the yeast-cells, from which they are separated by exosmosis, and amongst the other products are leucine and tyrosine. An experiment upon 350 grams of moist yeast, representing 84 grams of the dry substance, furnished 5 grams of leucine and 5 decigrams of tyrosine (*Compt. rend.* lxxi. 689; lxxiv. 184).

When the yeast which works off from new beer in cask during the process of cleansing is allowed to settle, the fluid portion removed, and water added to the remainder, nearly all the cells of yeast rise to the surface in three days, and under the microscope they are seen to move with the agility of the most active monads. These bodies resemble in size and shape the yeast-cells from which they have been derived, and their surface is covered with fine dark granules which appear to have resulted from an alteration of the superficial membrane (Trécul, *Compt. rend.* lxxiv. 23).

According to Hoppe-Seyler (*N. Rep. Pharm.* xx. 764) the ferment which converts cane-sugar into grape-sugar forms, when separated from beer-yeast, a white powder, which is soluble in water, and may be preserved unaltered in the dry state under alcohol. Living beer-yeast does not give it up to water, but if the yeast be killed by addition of a little ether, the ferment may easily be extracted by water and separated from the solution. The aqueous solution quickly effects the transformation of the sugar.

*Ash of Yeast.*—The ash of yeast has been analysed by Béchamp (*Compt. rend.* lxxiii. 337) with the following results:—

SO <sup>2</sup>	P <sup>2</sup> O <sup>3</sup>	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	Al <sup>2</sup> O <sup>3</sup>	SiO <sup>2</sup>
5.665	55.628	28.691	0.804	1.608	6.878	0.840	undetermined	= 100.114

Another experiment gave 5.771 p.c. SO<sup>2</sup>, 56.94 P<sup>2</sup>O<sup>3</sup>, and 6.94 MgO.

The incineration was effected by means of bismuth nitrate in the manner described under 'Ash of Organic Bodies' (p. 108).

On the origin and development of Bacteria and Vibriones, and their relation to Fermentation and Putrefaction, see BASTIAN (*Proc. Roy. Soc.* xxi. 129, 224, 325, 349).

**Antiferments or Antiseptic Substances.** *Mercuric oxide* completely prevents alcoholic fermentation, and likewise the conversion of cane-sugar into grape-sugar; cupric salts act in a similar manner. *Ferric salts* colour yeast dirty yellow; after two or three days, however, the colour disappears, and regular fermentation slowly sets in. The *chlorides of potassium* and *sodium* appear slightly to accelerate alcoholic fermentation. *Caustic alkalis*, added in sufficient quantity to produce strong alkaline reaction, do not interfere with it, but they render it imperceptible for some time by absorbing the carbonic acid. *Chloroform* prevents fermentation to a considerable extent, a few drops added to 100 c.c. of a fermenting mixture containing 5 p.c. sugar sufficing to arrest it. *Quinine* acts in the same way. *Nicotine* accelerates fermentation slightly; so does *strychnine* at first, but afterwards retards it. *Creatine* appears to retard fermentation, but is itself at the same time converted into creatinine, which accelerates it. *Hydrocyanic acid* retards fermentation, or arrests it completely; its action, however, does not extend to the yeast-water or only so far as to exert a preservative action upon it. The yeast when freed from the hydrocyanic acid regains its activity. This action of hydrocyanic acid upon yeast is similar to that which it was observed by Schönbein to exert on the colouring matter of the blood (Liebig, *Ann. Ch. Pharm.* cliii. 137).

Calvert (*Proc. Roy. Soc.* xx. 197) made a series of experiments on a solution of albumin to which was added one-thousandth part of an antiseptic substance. He found that such substances may be divided into four classes:—

1. Those substances which entirely prevent the development of protoplasmic life and of fungi: these are phenol and cresol.
2. Those which prevent the development of vibrios without stopping the production of fungi: zinc chloride, mercuric chloride, and zinc sulphophenate.
3. Those, on the contrary, which permit the production of vibrios and prevent that of fungi: lime, quinine sulphate, pepper, and prussic acid.
4. Those which do not prevent the production either of protoplasmic life or of fungi: sulphurous, sulphuric, nitric, arsenious and acetic acids; caustic potash, soda and ammonia; solution of chlorine; sodium, calcium, and aluminium chlorides; calcium hypochlorite; potassium chlorate; calcium sulphate; ferrous sulphate; calcium bi-

sulphate: sodium thiosulphate; sodium phosphate; calcium phosphate; potassium permanganate, potassium and sodium sulphophosphates; picric acid; turpentine; wood-charcoal.

Acids, while not preventing the development of vibrios, facilitate the production of fungi: this applies especially to sulphuric and acetic acids. Alkalies, on the contrary, are not favourable to the production of fungi, but favour the development of vibrios. Zincchloride and mercuric chloride completely prevent the development of animalcules, but do not stop the formation of fungi. Chlorine and calcium hypochlorite stop the production of vibrios only when employed in great excess; and when calcium hypochlorite is so used, it acts with violence upon the proteic matters, producing a disengagement of nitrogen. Quinine sulphate completely stops the formation of fungi, and this fact leads to the supposition that, as quinine sulphate is remarkably efficacious in cases of intermittent fever, this malady may be caused by the introduction into the human economy of fungoid bodies. This seems all the more probable when it is considered that this fever is most prevalent in swampy countries where there is much decomposition of vegetable matter. Wood-charcoal possesses no antiseptic properties: it absorbs the putrid gases produced and causes their oxidation.

According to Ralutau a. Papillon (*Compt. rend.* lxxv. 755) 1 p.c. of sodium silicate prevents the alcoholic fermentation of grape-juice. Urine containing 2 p.c. of the salt undergoes no decomposition, even in 15 days, and the evolution of ammonia is scarcely sensible with 1 p.c. Milk mixed with one-fourth of its volume of water containing one twenty-fifth part of the silicate, remains free from acidity at the end of five days, and if the cream be then removed, the remaining liquid will be found to be alkaline, and without a single flake of casein. An emulsion of three sweet and three bitter almonds made with water containing one twenty-fifth part of the salt is quite innocuous, and remains so at the expiration of ten days. It appears then that silicate of sodium, like borax, prevents fermentation and putrefaction, only its action is more energetic. 2 grams of borax dissolved in 40 grams of water, and injected into the veins of a dog, produced no appreciable effect upon the health of the animal; while an injection of 1 gram only of sodium silicate under the same conditions caused death. In the latter case the effects produced were purging and vomiting, and the urine contained albumin; the appetite gradually diminished, and the animal died in nine days.

Petit (*Compt. rend.* lxxv. 881) finds that when a solution of cane-sugar contains 1 p.c. of sodium silicate, fermentation commences slowly after the addition of the yeast, but when established it proceeds rapidly and very regularly. 1 p.c. of borax has no effect on fermentation. The same proportion of ferrous sulphate causes the fermentation to proceed slowly but regularly. With copper sulphate the fermentation commences, but soon stops. With 1 p.c. of arsenic trioxide the fermentation proceeds slowly, but very regularly.

Acetic acid is more antifermentative than the same quantity of a mineral acid. 1 p.c. of oxalic acid markedly slackens the rate of fermentation.

The most antifermentative bodies tried were mercuric oxide and chloride.

Sulphites do not hinder fermentation, and are themselves converted into sulphates as the fermentation proceeds.

*Function of Chalk in Butyric Fermentation.*—Béchamp finds that the addition of a drop or two of phenol or creasote to 100 c.c. of sugar-solution checks butyric but not alcoholic fermentation, and hence concludes that the butyric ferment is more easily killed than the more highly developed cell of beer-yeast. According to O. Loew, on the other hand (*Chem. News*, xxiii. 100), beer-yeast may also be destroyed by a sufficient addition of phenol; and its greater vitality is due simply to the relatively larger quantity of it compared with that of the butyric ferment, which is introduced into a sugar-solution from the air. Béchamp moreover finds in chalk a butyric ferment, which is not destroyed by phenol (*1st Suppl.* 614). According to Loew's experiments, this ferment does not exist in the chalk in its natural state, but is introduced from the air during pulverisation, and the inaction of phenol with regard to it is due to the absorption of the phenol by the chalk, so that to arrest the fermentation a considerable quantity of phenol is required. That marble excites fermentation in a liquid containing phenol less easily than chalk, arises not from the absence of microzymes, but from the inferior capacity of the marble to absorb phenol; for when phenol is not present, marble after exposure to the air excites the butyric fermentation just as well as chalk. The retardation of butyric fermentation by small quantities of phenol may also be prevented by addition of animal charcoal.

**FLUORENE**  $C_{13}H_{10}$ . A fluorescent hydrocarbon discovered in the portion of coal-tar boiling at  $300^{\circ}$ – $340^{\circ}$ , by Berthelot (*Ann. Ch. Phys.* [4], xii. 222), who, however, did

not assign any definite formula to it. It is best obtained by crystallising the portion which distils between  $300^{\circ}$  and  $305^{\circ}$  from a mixture of alcohol and benzene, whereby a quantity of acenaphthene is separated from it.

*Dibromofluorene*  $C^{12}H^8Br^2$  crystallises in beautiful monoclinic tables. When it is brought to a red heat in presence of lime, it yields a hydrocarbon melting below  $1000^{\circ}$ , and having the odour and appearance of diphenyl. Fluorene is, therefore, probably a diphenyl methylene  $C(C^6H^5)^2$ . *Fluorene picrate* crystallises in fine red needles, melting at  $80^{\circ}$ – $82^{\circ}$ , and having the composition  $C^{12}H^{10}.C^6H^3(NO^2)^2O$  (Barbier, *Compt. rend.* lxxii, 442).

**FLUORESCIN**  $C^{20}H^{12}O^3$ . This substance, the phthalcin of resorcin, is obtained by heating resorcin and phthalic anhydride together at  $195^{\circ}$ . It crystallises from alcohol in brown crusts, and is precipitated by acids from its alkaline solution as a brick-red powder. By treatment with zinc-dust in an alkaline solution it is reduced to colourless fluorescein, which is the phthalin of resorcin. When strongly heated with sulphuric acid, fluorescein yields a red body which dissolves in alkalis with a blue colour. This red-solution dyes blue like indigo, but the colour is neither so fine nor so fast (A. Baeyer, *Deut. Chem. Ges. Ber.* iv, 658).

**FODDER-PLANTS.** Under this head we treat of those forage plants which are not noticed under their respective names. Fodder crops are always cut while green, and before the formation of seed, and are either consumed by cattle in the fresh state, or made into hay. The composition of all these crops is, from their immature condition, subject to a far wider range of variation than the composition of grain crops, which are not harvested till the functions of the plant are completed.

The composition of a fodder crop may be said to depend—1. On its age, and the relative development of its parts; 2. On the composition of the soil in which it grows; 3. On the special characters belonging to its species. With crops harvested in a perfectly mature condition, the element of species has a preponderating effect on the composition, and the nature and richness of the soil have a smaller influence. With fodder crops, on the other hand, it is the state of development of the plant which most determines its composition, and the nature and richness of the soil have a large effect, while the special characters due to the particular nature of the plant are often so effectually hidden by the large influence of the two first-named conditions, that it becomes a task of great difficulty to ascertain what is the intrinsic difference between two fodder plants.

The proportion of water in a plant is greatest when young, and decreases during its growth.

The percentage of nitrogen in the dry plant decreases considerably during growth; this is true not only of the whole plant, but of all its parts, save the blossom, which increases in nitrogen as ripening commences. The diminution of nitrogen in the whole plant is, however, largely due to the alteration of the proportion of its parts as growth proceeds. In an immature plant the leaf is the part richest in nitrogen; a plant in its youngest condition consists principally of leaves, and at this period the plant contains its highest percentage of nitrogen; as the stem, which is poor in nitrogen, is developed, the percentage of nitrogen in the plant falls. The fall in the whole plant is thus more rapid in the earlier stages of its growth than in any of its parts.

The percentage of ash in the dry substance of the plant decreases considerably with age; while, however, the ash falls in the whole plant, it rises in the leaves as the plant matures. The percentage of fat also diminishes with age. Fat occurs in greatest quantity in the leaf, and its proportion in the whole plant diminishes with the growth of the stem.

The percentage of carbohydrates in the dry substance, on the other hand, increases considerably during growth; there is especially a large formation of cellulose as the plant matures, a fact which has great influence in determining the nutritive value of a fodder crop.

These facts are well illustrated by the following table, which shows the composition of plants taken at different dates from the same field. The analyses of Grass from a water-meadow were by Way (*Jour. Roy. Agri. Soc.* xiv, 171); the analyses of Vetches by Ritthausen (*Jahresb. Agr. Chemie*, 1859–60, 79); the analyses of Lucerne by Kühn (*Landw. Versuchs-Stationen*, xvi, 86); and the analyses of Red Clover by E. Wolf (*Ann. d. Landwirtschaft*, 1871, 130). The table states the composition of the dry plant, and, where the information is obtainable, the percentage of water in the fresh plant is also given.

	Grass		Vetches				Lucerne		Red Clover			
	April 30	June 26	May 23	June 12	June 23	July 12	June 4	June 15	Young	June 13	June 23	July 20
Albuminoids .	25.9	10.9	28.8	19.7	16.3	15.9	18.3	17.8	21.9	13.8	11.2	9.5
Fat . . . .	6.5	2.1	35.7	37.2	41.1	31.6	3.2	2.4	43.6	46.2	50.1	43.2
Extractive matter . . .	32.1	43.9										
Fibre . . .	25.1	34.3	23.9	33.5	32.7	45.3	25.8	32.4	24.7	32.8	32.9	41.7
Ash . . . .	10.4	8.8	11.6	9.6	9.9	7.2	9.6	8.0	9.8	7.2	5.8	5.6
Water fresh . . .	87.6	74.5	83.7	83.2	82.9	80.6	78.0	76.0	—	—	—	—

The composition of the ash of a plant also undergoes alteration during growth. The analyses of the ash of the water-meadow grass just referred to have been already given in this Dictionary (see 'Grass,' vol. ii. 943); the increase of silica in the older grass, and the diminution of potash, are very striking. The changes which take place in the ash of graminaceous crops during growth will be noticed in detail under 'Oats' and 'Wheat' in the present volume; we will here give some of the results of Ulbricht's elaborate investigation on Red clover (*Landw. Versuchs-Stationen*, iii. 241, and iv. 1). Ulbricht examined clover grown on arable land, and clover grown in a garden soil; both the first and second crops were in each case the subject of investigation. Samples of each of the four crops were taken in several stages of growth: 1. At the first appearance of stem formation; 2. At first appearance of flower buds; 3. At full blossom; 4. When the seed was ripe. At each of these stages the various parts of the plant were separately analysed. The results yielded by the first crop on the garden soil, and the first crop on the field soil, are given in the table on page 526.

It will be noticed that in several points the results obtained in the poor and rich soil are very different, but the following general facts are evident:—

Clover increases in dry substance during growth; the leaves are the driest part till the blossom is matured. The proportion of ash in the dry substance diminishes as growth proceeds. In the young plant the leaf-stalk and stem contain most ash; the ash in the stem, however, rapidly decreases, while the ash in the leaf increases, so that at full bloom, and afterwards, the leaf surpasses all other parts in its contents of mineral matter. In the young plant potash is found chiefly in the leaf-stalk and stem, and in much smaller quantity in the leaf. The stem contains but little lime in proportion to its potash, but the leaf contains much lime in proportion to its potash (the same is true of graminaceous plants), and the amount of lime in the leaf steadily increases as the plant matures. The increase of lime and magnesia during the maturation of leguminous plants has been also noticed by Ritthausen. Phosphoric acid has its first maximum in the leaf, but after the formation of blossom it concentrates in this part of the plant. Silica, as with graminaceous plants, is found in greatest quantity in the leaf. Chlorine is at first chiefly located in the stem and leaf-stalk, and afterwards in the blossom. Nitrogen and sulphur find their maximum in the leaf till the blossom has become ripe, which then surpasses the leaf in nitrogen, and perhaps in sulphur.

Hellriegel (*Landw. Versuchs-Stationen*, iv. 31) has shown that the amount of the various ash-constituents present in the sap varies with the age of the plant. Experimenting on the clover crops used by Ulbricht, he found that the amount of potash existing dissolved in the sap was greater in the leaf than in the stem, and diminished in all parts by age. In the leaves of a very young plant 75 p.c. of the potash present was found in solution, but at full blossom only 37 p.c. was found dissolved in the leaves, and 15 p.c. in the stem. Lime, on the other hand, did not diminish in solubility as the plant matured, about 70 p.c. of the contents of the leaves being uniformly soluble, and about 50 p.c. in the stem. Magnesia, save in the case of the very young plant, exhibited the highest solubility of all the bases. Of phosphoric acid only about 20 p.c. was found in solution in the leaves, but rather more in the stem; its solubility was not altered in any marked degree by age. In the very young leaves 27 p.c. of the silica was found in solution; at full bloom this had fallen to 16 p.c. It is notable that at blooming time the blossom contained more soluble potash, phosphoric acid, and silica, than any other part of the plant. It appears that at those times, and in those organs in which the process of formation proceeds most vigorously, there the active ingredients of plant-food are most abundantly present in a soluble form.

**RED CLOVER.—Composition of Individual Parts, and of Whole Plant, per 10,000 Parts of Dry Substance; also Water in 10,000 Parts of Fresh Substance.**

	First Crop, Garden Soil										First Crop, Field Soil																			
	Period I., April 30					Period II., May 23					Period III., June 21					Period II., May 29					Period III., June 23					Period IV., End of August				
	Leaf-Stalk	Whole Plant	Stem	Leaf-Stalk	Whole Plant	Leaf-Stalk	Stem	Whole Plant	Leaf-Stalk	Whole Plant	Leaf-Stalk	Stem	Whole Plant	Leaf-Stalk	Stem	Whole Plant	Leaf-Stalk	Stem	Whole Plant	Leaf-Stalk	Stem	Whole Plant	Leaf-Stalk	Stem	Whole Plant	Leaf-Stalk	Stem	Whole Plant		
Nitrogen	313.1	534.9	419.8	232.0	384.9	534.4	333.0	—	163.7	233.9	457.9	378.5	523.3	179.6	277.1	338.6	290.3	126.4	204.3	344.5	314.9	227.3	124.3	202.0	201.4	88.70	—	239.4		
Sulphur	—	39.5	—	16.1	—	41.3	—	—	11.9	26.4	36.1	22.7	18.5	—	—	40.6	—	—	—	—	—	—	—	—	—	—	—	—		
Potash	683.6	332.3	481.2	246.9	609.1	302.7	477.9	314.7	510.1	111.8	218.0	378.5	540.9	407.8	172.8	352.9	382.9	54.3	136.7	225.8	159.2	112.9	19.5	57.7	38.7	112.7	68.4	—		
Soda	53.2	17.7	31.3	10.2	13.7	15.8	12.9	10.6	16.1	22.2	19.2	13.9	14.6	8.0	—	6.8	8.7	12.2	2.4	1.2	5.8	10.0	none	11.6	4.7	7.5	—	—		
Lime	100.0	268.7	23.6	113.6	189.7	288.5	109.1	100.5	219.1	35.5	148.8	157.5	161.5	27.5	322.6	267.0	95.9	282.3	305.7	139.1	212.8	119.3	305.4	430.4	132.3	178.1	—	—		
Magnesia	91.1	65.5	78.3	61.7	82.6	71.0	69.6	39.3	56.6	86.2	56.8	67.8	74.3	88.6	63.5	72.4	68.5	113.0	22.9	48.1	72.1	89.0	129.0	110.7	103.4	163.3	—	—		
Ferric oxide	5.7	10.2	8.3	4.0	10.7	6.3	6.3	2.9	11.0	12.6	17.6	6.7	7.4	10.5	11.0	9.6	6.3	15.5	5.9	8.9	7.6	8.2	18.4	16.2	10.4	16.3	—	—		
Phosphoric acid	163.2	141.5	149.3	113.1	134.7	123.1	121.3	73.3	113.2	87.9	116.8	83.2	89.6	99.6	115.7	98.8	28.3	58.5	61.8	90.6	63.1	23.0	21.9	25.8	63.3	57.4	—	—		
Sulphuric acid	3.6	none	1.4	31.0	7.0	none	15.1	7.9	trace	none	trace	4.9	16.3	3.8	none	6.7	trace	trace	1.3	1.3	4.4	—	—	—	—	—	—	—		
Silica	10.8	12.7	12.6	1.9	4.3	10.3	5.3	9.6	6.5	11.9	14.8	4.6	4.7	7.9	9.8	6.0	2.2	1.6	12.0	1.3	4.4	1.7	13.4	13.1	13.5	7.8	—	—		
Chlorine	43.8	9.6	22.7	41.3	45.6	13.1	34.6	27.9	38.8	23.7	33.1	28.5	32.1	28.3	6.3	29.1	17.4	84.4	15.7	33.7	22.9	6.1	20.3	3.8	14.0	9.8	—	—		
Ash	1238.1	379.0	1016.9	915.3	1086.9	532.6	925.3	631.4	962.7	736.4	617.6	722.1	922.4	911.5	739.1	835.7	278.2	639.4	829.1	542.8	489.9	269.8	606.7	909.5	438.1	417.0	—	—		
Water in 10,000 of fresh sub.	8865	8268	8535	8781	8760	8258	8645	8240	8749	8191	8333	8319	8300	8591	7900	8312	7093	7775	7090	7010	7147	1377	858	921	717	1076	—	—		

Percentage Composition of Ash.																												
Potash	54.8	40.3	47.1	59.3	55.5	36.2	51.2	53.8	52.5	41.3	34.9	52.0	58.1	44.4	23.6	42.0	19.4	23.2	14.9	39.0	22.9	7.3	9.4	4.3	30.9	16.3	—	—
Soda	4.3	2.0	3.1	1.1	1.3	1.5	1.4	1.7	1.7	2.2	3.1	1.9	1.3	1.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Lime	15.2	30.5	23.8	12.3	17.3	31.0	20.4	15.8	22.6	33.8	23.8	21.6	17.4	20.7	43.7	31.8	34.0	41.9	61.4	24.7	43.2	43.2	40.0	50.0	7.4	28.7	42.5	—
Magnesia	7.6	7.4	7.3	6.7	7.3	8.5	7.3	6.2	5.8	8.7	9.1	7.0	8.0	9.6	8.7	8.6	24.3	16.8	11.3	9.4	14.8	33.1	20.6	12.2	10.6	13.7	—	—
Phosphoric acid	13.1	16.1	14.7	12.2	12.2	14.7	15.0	11.3	11.6	8.9	18.7	11.4	8.9	9.9	15.8	11.3	10.0	8.7	7.5	17.8	10.8	9.2	11.8	8.1	20.2	13.7	—	—
Sulphuric acid	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica	3.3	1.1	2.3	4.4	4.2	2.3	3.7	4.4	4.4	2.4	3.3	3.3	3.3	3.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Chlorine	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

*Percentage Composition of Ash.*

	Potash	Soda	Lime	Magnesia	Phosphoric acid	Sulphuric acid	Silica	Chlorine
Potash	54.8	40.8	47.1	59.3	55.5	36.2	51.2	53.8
Soda	4.3	40.8	3.1	1.1	1.3	1.9	1.4	1.7
Lime	15.2	30.5	23.3	12.3	17.3	31.5	20.4	15.6
Magnesia	7.6	7.4	7.3	6.1	7.5	8.5	7.9	6.2
Phosphoric acid	13.1	16.1	14.7	12.2	12.3	14.7	13.0	11.6
Sulphuric acid	3.0	none	3.1	2.4	6.0	none	1.0	1.2
Silica	3.5	1.1	2.3	4.3	4.2	2.3	3.7	4.4
Chlorine	—	—	—	—	—	—	—	—

Carbonic acid, acid, and chlorophyll are not included in the ash. The oxygen equivalent of the chlorine is deducted. 1. Ferric oxide and sulphuric acid included in the ash. 2. Weight of the substance.

Voelcker (*Jour. Roy. Agri. Soc.* 1867, 30) determined the composition of clover at different stages of growth, and also the total amount of the dry substance that was soluble in water. On June 2, the soluble matter was 41.04 per cent.; this steadily fell, and on July 28 it amounted to only 29.27 p.c. The changes in the composition of fodder crops by age are clearly of such a nature as to diminish their nutritive value; crops cut for hay, should, therefore, not be allowed to pass the commencement of full blossom; the maximum amount of nutritive matter is probably then obtained, but rapid deterioration follows if the crops are allowed to become older.

As already stated, the composition of fodder crops is largely influenced by the nature of the soil, and of the manure employed. On a rich soil, producing luxuriant growth, fodder crops will be found to contain more water, more ash, more nitrogen, and more fat, than the same crops growing less rapidly, on a poorer soil. The tendency of high manuring is, in fact, to produce a great bulk of immature produce. We cannot better illustrate the effect of manure in altering the composition of green crops than by quoting some of the results obtained at Rugby by sewage irrigation on meadow land, and published by the Royal Commissioners, Messrs. Lawes and Way, in their report. The following table shows the composition of the sewaged and unsewaged grass in 1863. The grass was cut for green food throughout the year, each cutting being separately analysed; from these analyses the average composition of the whole produce from each plot has been calculated. The produce is, for the purpose of comparison, reckoned as hay containing 15 per cent. of water; the average amount of water in the fresh grass is also given.

*The quantity and composition of Meadow Grass grown with and without Sewage, the grass reckoned as Hay containing 15 p.c. of Water.*

Tons of sewage per acre per annum . . .	} none	3,000	6,000	9,000
Weight of hay in tons per acre . . .	} 2.08	5.15	6.04	6.98
Per cent. of water in fresh grass . . .	} 61.25	80.32	85.20	83.98
Water . . . . .	15.00	15.00	15.00	15.00
Albuminoids . . . .	7.34	13.43	17.16	18.57
Fat . . . . .	2.87	4.36	4.16	4.03
Fibre . . . . .	24.96	21.94	21.55	22.23
Extractive matter . .	42.06	36.46	32.83	30.68
Ash . . . . .	6.87	8.81	9.30	9.49
	100.00	100.00	100.00	100.00

The amount of nitrogen in the sewaged grass was in individual cases as high as 25.27 p.c. of albuminoids in the hay. In the case of green crops grown with sewage, we have the effect of manure in its most striking form; manures applied to a dry meadow have a less marked effect on the composition, and the effect is further diminished if the crop is allowed to grow to its full extent before being cut; the excess of soil-food under these conditions has time to discharge its proper functions, and determine a greater assimilation of carbon from the atmosphere, and the result of manuring appears in the quantity rather than in the quality of the crop. Messrs. Lawes and Gilbert have kindly supplied the writer with an abstract of the composition of the meadow hay obtained in experiments conducted for 18 years at Rothamsted; during this period the same manures have been applied each year to the same plot. The results are shown in the table on page 532.

With the increasing bulk of the crop we see that there is a small increase in the amount of water in the hay. The ash of the hay is greater wherever ash-constituents have been supplied in the manure; it is greatest where ash-constituents have been applied alone, and therefore relatively in greatest excess, and least where the crop has been increased by the use of ammonia, without any ash-constituents having been applied for 18 years. With regard to the nitrogen in the crop the case is somewhat complicated. The nitrogen is highest, as we should expect, where ammonium salts have been applied alone, and where nitrogen is, therefore, in great excess of all the

Percentage composition of Hay grown on experimental plots in Rothamsted Park during 18 years—1856-73.

	No Manure	Ammonium Salts 400 lbs.	Mixed Cinereal Manure	Cinereals, and Ammonium Salts 400 lbs.	Cinereals, and Ammonium Salts 800 lbs.
Average produce in cwt. per acre	28½	27½	35½	52½	60½
Dry matter :—					
Highest	88.50	87.46	87.68	87.07	86.13
Lowest	79.00	79.01	78.47	78.95	76.92
Average	84.03	83.48	83.71	82.44	81.18
Ash in dry :—					
Highest	7.97	8.06	8.67	8.58	8.41
Lowest	5.59	4.75	6.49	5.71	5.89
Average	6.83	5.85	7.71	7.11	7.23
Aluminoids in dry :—					
Average	10.52	13.48	10.90	9.64	12.16

other food-constituents, but it is not lowest on the plots receiving no nitrogen. This is partly due to the fact that on the plot receiving only cinereals (a mixture of superphosphate with salts of potassium, sodium, and magnesium), and to a less extent on the unmanured plot, there is a considerable amount of leguminous herbage, which is not found on the other plots. Leguminous plants are far more nitrogenous than the grasses, and hay containing some clover will, other things being equal, contain more nitrogen than grass hay. The hay on the plot receiving cinereals and 400 lbs. of ammonium salts appears to stand lowest as to nitrogen because it is a purely grass-hay, but still more because the crop, under the influence of a liberal manure supplying no excess of nitrogen, is here better matured, tending more to stem and flower than on the unmanured plot. When the ammonium salts are doubled, as in the next plot, and the nitrogen supply becomes excessive, the percentage of nitrogen in the hay rises at once. There can be little doubt that if the grass crops at Rothamsted were cut in a less mature condition, the differences in their composition would be found to be far more considerable. The same amount of food which is only adequate for a large full-grown plant is excessive for a young, and therefore small, plant.

The composition of the ash of a fodder crop is greatly influenced by the nature of the soil. The ash of a perfected seed is very constant in its composition, whatever be the manure applied, but the ash of a green plant is greatly affected by the nature of the soluble matters in the soil; a luxuriantly growing plant contains in fact an excess of many of the ash-constituents which it requires. The alteration in the composition of the ash resulting from differences in the soil, or in the manure, will be best illustrated by giving the ash analyses of some of the experimental hay crops at Rothamsted already described. The analyses represent the average composition of the ash in three successive years, 1856-8 (*Jour. Roy. Agri. Soc.* 1859, 398), they are here recalculated to 100 parts, omitting charcoal and sand.

It is seen that wherever potash was applied the amount in the ash is about one-half more than in the ash of the crops receiving no potash. Also wherever ammonium salts (mixed sulphate and chloride) were employed, the ash becomes exceedingly rich in chlorine. Phosphoric acid is increased in every case where it was applied, but only to a small extent. This increase, both of base and acids, resulting from the manure, is accompanied by a corresponding falling off in lime and silica. The high carbonic acid and low silica in the ash of hay manured with cinereals only is due to the large amount of leguminous herbage present.

A further instance of the influence of soil on the composition of the ash will be found on comparing the ash analyses of clover grown in a garden and field soil already given; the clover from the field is far richer in lime and magnesia, and much poorer in potash than clover of the same age from the garden soil. Kreuzhage (*Jahresb. Agr. Chem.*, 1866, 270) gives ash-analyses of clover manured with various salts. There is an increase of potash, soda, phosphoric acid, and chlorine, where these were applied, but no increase of lime or magnesia followed their application. The extent to which potash and lime can be substituted for each other in green clover is very great, the



*Analysis of the Ash of Meadow Hay variously Manured.*

	No Manure	Ammonium Salts, 400 lbs.	Mixed Cereal Manure	Cereals, and Ammonium Salt 400 lbs.	Cereals, and Ammonium Salts 800 lbs.
Potash . . .	21.30	18.18	30.79	29.75	30.32
Soda . . .	8.83	10.96	4.73	7.47	8.91
Lime . . .	15.73	14.75	13.86	10.20	9.10
Magnesia . . .	4.34	5.00	3.82	3.61	4.17
Ferric oxide . . .	.13	.12	.32	.47	.51
Phosphoric acid . . .	5.09	4.94	6.80	6.67	6.26
Sulphuric acid . . .	6.38	8.04	8.05	6.64	6.00
Chlorine . . .	6.52	15.59	6.74	17.47	20.92
Carbonic acid . . .	5.89	3.41	6.86	1.98	1.81
Silica . . .	27.17	22.52	19.46	19.68	16.68
	100.00*	100.00*	100.00*	100.00*	100.00*

\* The oxygen-equivalent of the chlorine is here deducted.

percentage of potash in the ash ranging from 15-40, and the lime varying as greatly in an inverse direction. The same is true of other leguminous fodder crops. The plant seems to take potash by preference when it can get it, and to assimilate lime as a substitute. It is thus well established that the composition of the ash of green crops is, within certain limits, largely dependent on the nature of the soil and of the manure applied.

The influence of climate and season on the composition of fodder crops is mainly one affecting their maturity. In a cold wet season blossoming is retarded, and takes place but partially; the crop then has a composition proper to a less mature condition than when the season is dry and warm, and blossoming takes place earlier and more abundantly. The great influence of season in this respect has been already illustrated, as far as the proportion of ash is concerned, by the table showing the composition of the hay grown at Rothamsted during eighteen years; it will be seen that the percentage of ash in the hay is influenced to a greater extent by season than by manure; the same is true of the variations in nitrogen, which the table does not supply.

We come now to the last element in the composition of fodder crops, namely, the characters proper to the different species. What has been already said concerning the vast influence of age, soil, and season on the proportion of the constituents of a green plant, makes it very clear that to distinguish accurately between different older crops they must all be grown under precisely similar conditions, and harvested at the same stage of development. Different investigators have taken pains that some of the necessary conditions should be uniform in the plants they selected for analysis, but no investigator seems to have succeeded in insuring the presence of all the conditions required for an exact comparison. The results of different investigators are also seldom comparable, working as they necessarily have done in different soils and seasons. It is impossible, therefore, to prepare a table which shall compare exactly the composition of fodder crops; all that can be done is to call attention to some general principles which determine differences between different species, and to give some averages of analyses of the more ordinary crops, harvested at the time of blossoming.

Leguminous crops contain in all their parts a considerably larger amount of nitrogen than graminaceous crops; they also yield a larger amount of ash. It is quite possible, however, that an immature, richly manured graminaceous crop may contain more both of nitrogen and ash than a mature leguminous crop. The two great classes of leguminose and graminaceæ include nearly all the fodder crops; to distinguish between the characters of the different species in these two classes we cannot do better than notice the habit of the plant. A plant the character of which is to produce a large proportion of leaf to stem will contain more nitrogen than a plant of the same habit which is to produce smaller or fewer leaves. Thus, as Aрендt and I have observed, such grasses as *Briza media* and *Lolium perenne* will always stand amongst the less nitrogenous grasses, while grasses of such habit as *Holcus lanatus* and *Bromus mollis* will rank amongst the more nitrogenous. In the same manner *Festuca repens* must stand amongst the most highly nitrogenous clovers, and *Trifolium* 2nd Sup.

*folium incarnatum* will rank with those containing least nitrogen. The woody fibre will follow an inverse order to the nitrogen, and will be more abundant in stemmy than in leafy herbage. As the leaf is the driest part of the plant, a plant with abundant foliage will evidently contain less water than another of the same class which runs to stem. Similar reasoning might probably be applied to other ingredients if our knowledge were more extended: thus Arendt and Knop observe that leafy grasses or sedges contain considerably more silica than others which have a greater proportion of stem; in making this comparison, however, it must be recollected that the more luxuriant the plant, the less silica will it contain. A leafy grass, according to the same observers, will also contain 2-3 times as much lime as magnesia, while grasses with leaves close to the stem contain these bases in nearly equal proportions.

The following investigations have been made on the composition of individual species. Way (*Jour. Roy. Agri. Soc.* 1853, 171) has published full analyses of 19 grasses, 11 leguminous fodder crops, and 10 weeds and meadow-plants all collected when in blossom. The most nitrogenous grass was *Bromus mollis*, containing 17.29 p.c. of albuminoids in the dry state; the least nitrogenous was *Briza media*, containing 6.08 p.c. The most nitrogenous leguminous plant was *Vicia sativa*, containing 23.61 p.c.; and the least nitrogenous, *Melicago sativa*, containing 12.76 p.c. of albuminoids in the dry state. Amongst the weeds, *Poterium Sanguisorba* and *Plantago lanceolata* were the most nitrogenous, containing respectively 16.75 and 14.29 p.c. of albuminoids. Way's ash-analyses of these plants have been already given in this dictionary; see 'Fodder' and 'Grass' (ii. 630, 943).

Ritthausen and Scheren (*Jahresb. Agr. Chemie*, 1859, 76) have published complete analyses of 21 grasses and 8 leguminous plants gathered at the time of blooming. The most nitrogenous grass was *Alopecurus geniculatus*, containing 13.0 p.c. of albuminoids; and the least nitrogenous, *Phleum pratense*, containing 6.3 p.c. of albuminoids in the dry state. The most nitrogenous leguminous plant was *Vicia cracca*; the least nitrogenous, *Trifolium pratense*; they contained respectively 24.0 and 14.28 p.c. of albuminoids in the dry.

Arendt and Knop (*Landw. Versuchs-Stationen*, 1860, 32) have given analyses of 22 grasses, and of 10 sedges and rushes, nearly all at the time of blooming; they determined the nitrogen, and some of the ingredients of the ash. Among the grasses *Holcus lanatus* was the most nitrogenous, containing 17.6 p.c. of albuminoids, and *Festuca elatior* and *Agrostis Spica Venti* the least nitrogenous, both containing 7.4 p.c. of albuminoids in the dry. Of the sedges, *Carex acuta* contained 16.4 p.c., and *Carex vulpina* 12.2 p.c. of albuminoids, these being respectively highest and lowest. *Juncus conglomeratus* yielded 13.5 p.c. of albuminoids. The ash in the whole series ranged from 13.7 to 5.7 p.c., the highest ash being given by *Carex remota*, and the lowest by *Juncus conglomeratus*. The ash of the true grasses ranged from 9.58 to 6.0 p.c., *Hordeum marinum* yielding the highest, and *Glyceria aquatica* the lowest ash.

The following table exhibits the average composition of various fodder crops when in full blossom; the analyses are calculated as hay containing 15 p.c. of water. The figures given for Meadow-hay are the mean of more than 50 analyses, and represent hay of good quality. The figures for Red Clover are the mean of 11 analyses, and fairly represent the composition of good clover hay. The remaining figures are in each case the mean of only a few analyses, and are less trustworthy. The ash given is with carbonic acid deducted:—

	Water in Fresh	Water in Hay	Albumi- noids	Fat	Non-nitro- genous Extractive Matter	Woody Fibre	
Grasses, mean of 18 species (Way)	68.8	13	9.4	2.6	38.8	28.5	5.7
Grasses, mean of 21 species (Ritthausen and Scheren)	70.8	15	7.8	2.1	35.1	34.0	6.0
Meadow hay		15	9.2	2.8	41.0	25.8	6.2
Red clover	78.0	15	11.2	3.1	37.2	24.8	5.7
White clover	80.0	15	15.7	3.6	36.7	22.1	6.9
Trefoil	80.0	15	15.7	3.3	34.4	25.8	5.8
Vetches	82.0	15	14.5	2.6	35.2	26.9	6.8
Lucerne	74.0	15	14.5	2.5	34.8	26.7	6.1
Sainfoin	79.0	15	13.9	2.6	34.7	28.7	6.1
Crimson clover	82.0	15	12.9	3.0	30.8	32.2	5.1
Kidney vetch	83.0	15	9.5	2.4	39.5	28.6	5.1

The higher amount of fibre in the grasses than in the meadow hay may partly be due to different methods of analysis, which, in case of the determination of fibre, have varied greatly; but probably the difference arises chiefly from the fact that meadow hay contains a good deal of young undergrowth, which would not be included in the flowering grasses selected for analysis. After-math (autumnal) hay is richer in nitrogen than the first crop, the season being less favourable to the maturity of the plant. It is seen from the table that meadow grasses contain less water than the clovers, when both are compared at the time of blossom.

The composition of the ash of fodder crops is subject, as already seen, to so wide a range of variation that it would only be misleading to quote analyses in cases in which no general average is obtainable; we give therefore only ash-analyses of meadow hay and of red clover hay. The analyses are in each case the mean of a large number:—

	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	Cl	SiO <sup>2</sup>	CO <sup>2</sup>
Meadow hay	26.95	5.70	13.45	4.82	.45	6.06	5.17	7.73	27.53	3.07
Red clover hay	26.31	1.22	25.93	9.30	.57	7.55	2.28	2.82	2.05	22.77

The characteristic difference between the ashes of leguminous and graminaceous fodder crops is the nearly entire absence of silica in the former, and the presence of a large quantity of carbonic acid. It is the practice of German chemists to deduct this carbonic acid and recalculate the ash to 100 parts. This plan has occasional advantages, but it entirely destroys the characteristic feature of the ash, and the relation of the ash-analysis to the amount of ash yielded by the plant, thus introducing much confusion if full details are not given. The ashes of the other leguminous fodder-crops are very similar to that of red clover, and subject to the same violent fluctuations in the lime and potash.

From the above data it is easy to calculate the quantities of nitrogen and of ash constituents which ordinary crops of hay remove from the soil. Taking the average crop of meadow hay at 1½ ton, and of clover hay at 2 tons per acre, the quantities removed by these crops will be in pounds per acre:—

	Nitrogen	K <sup>2</sup> O	CaO	MgO	P <sup>2</sup> O <sup>5</sup>	SiO <sup>2</sup>	Total Ash
Meadow hay, 1½ ton	49.3	56.3	28.1	10.1	12.7	57.5	209
Clover hay, 2 tons	101.6	87.4	86.1	30.9	25.1	6.8	332

The composition of hay does not differ from that of the plant from which it is made if the drying is carefully and quickly conducted; the finer parts of the plant are, however, apt to be broken off in hay-making, so that the percentage of albuminoids will often be a little lower, and of fibre a little higher in the hay than in the green crop. When hay suffers from rain in the field, there may be a considerable loss both of soluble ash and albuminoids (see Boyer, *Jahresb. Agr. Chemie*, 1867, 257). The amount of water in hay is subject to much variation. In the Rothamsted Park hay the extremes are 11.5—23 p.c.; this will be about the range in good hay. Clover hay generally contains rather more water than meadow hay.

The changes which hay undergoes in the rick have been little studied. The active fermentation which takes place in damp hay and results in the well-known heating of the rick and change of colour in the hay is accompanied, according to Voelcker (*Jour. Roy. Agri. Soc.* 1867, 30), by a great loss of sugar and other soluble carbo-hydrates, and also of soluble albuminoids, while aldehyde and acetic acid are among the products. According to Hösäus (*Jahresb. Agr. Chemie*, 1867, 258) ammonia is also formed. The loss of organic matter in dark brown hay is shown by its high percentage of ash. It has been supposed that the fibre of the hay becomes more digestible by fermentation in the rick, but there are no experiments which show that its solubility is thereby increased. The small amount of heating that takes place in well-made hay is probably without material effect on its composition.

The nature of the fat of hay has been made the subject of a special investigation by König and Kicsow (*Landw. Versuchs-Stationen*, xlii. 241; xvi. 40 and 47. *Deut. Chem. Ges. Ber.* vi. 500). The fat from meadow hay, when purified from chlorophyll by treating the ethereal solution with animal charcoal, amounts to about 1.52 p.c. of the dry substance, that from clover hay amounts to 1.61 p.c. (see table B, p. 506). This

fat is separated, by solution in boiling absolute alcohol, into a waxy substance which is deposited on cooling, and into a fluid fat which remains in solution. König first regarded the fluid fat as a true glyceride, but E. Schulze (*Landw. Versuchs-Stationen*, xv. 81) has shown that the fat of hay yields no glycerin. König and Kiesow have now ascertained that the waxy matter contains ceryl alcohol, cholesterol, and a hydrocarbon melting at  $65^{\circ}$ – $66^{\circ}$ , and having the percentage composition 84.96 carbon and 15.28 hydrogen; this agrees with the formula  $C^{20}H^{42}$ , but the new body is possibly cerotene,  $C^{21}H^{44}$ . Cerotic acid, and various unidentified members of the acrylic series, were also found in the fat from the hay.

**Method of Analysis.**—The analysis of fodder is effected on the partially dried substance. Water and ash are determined in the usual way, the ignition for ash being conducted at as low a temperature as possible. Fatty matters are separated by extracting the dry substance with ether till no more soluble matter is removed. The ethereal solution may be purified from chlorophyll by treatment with animal charcoal, but some loss is suffered in this operation, as the charcoal, even when well washed, retains a little of the fat. The ether is finally evaporated and the residue dried and weighed. The nitrogen is generally determined by combustion with soda-lime, and the amount of total albuminoids calculated from the nitrogen found. For this purpose the nitrogen is by different chemists multiplied by numbers ranging from 6.25–6.33, according to the view taken of the general composition of albuminoids. The lower number is most generally employed on the continent. It is very probable that in an immature plant, containing materials not yet fully elaborated, the whole of the nitrogen is not present as albuminoids, but exists partially in a lower form. The subject has been little studied, but it is well known that vetches and other plants contain asparagine (Cossa, *Gazzetta chimica italiana*, i. 683), and leucine (Morup-Besanz, *Deut. Chem. Ges. Ber.*, vii. 146), and that green crops grown by sewage contain nitrates (Müller, *Landw. Versuchs-Stationen*, xvi. 241). In the absence, therefore, of exact determinations, it must not be supposed that the nutritive value of highly manured crops necessarily rises with the rise in nitrogen.\* The determination of vegetable fibre presents peculiar difficulties. The fibre present is at least of two kinds, cellulose  $C_6H_{10}O_5$ , and lignose, a substance which encrusts the cells and contains about 10 p.c. more carbon than cellulose. These bodies are differently acted on by reagents; thus, purified cotton (cellulose) is almost completely dissolved by sulphuric acid, sp. gr. 1.53, when allowed to remain in contact for many hours, while cork and other tissues rich in lignose are scarcely acted on. On the other hand, digestion in the cold with nitric acid, sp. gr. 1.10, and potassium chlorate (F. Schulze's method), dissolves lignose pretty readily, but has little effect on cellulose (Church's *Laboratory Guide*, 3rd edition, 196). For some account of the very various methods that have been employed in determining fibre, see Pillitz (*Zeitschr. anal. Chem.* xi. 46). The plan most usually employed is that of Henneberg and Stolman. 3 grams of the dry substance in coarse powder are mixed with 150 c.c. of water and brought to boiling; 50 c.c. of sulphuric acid containing 5 p.c. of oil of vitriol are then added, and the whole is boiled for half an hour, water being added to maintain the volume at 200 c.c. The whole is allowed to cool, the clear liquid syphoned off, and the residue transferred to a weighed filter and well washed with hot water. The fibre is then returned to the beaker, and the original operation repeated, substituting for the sulphuric acid 50 c.c. of a 5 p.c. solution of sodium hydrate. After boiling for half an hour a considerable volume of cold water is added, and after standing the clear liquor is syphoned off, the fibre collected on the weighed filter, washed first with hot water, then with a few drops of hydrochloric acid, then well washed with water, and finally with a 1 p.c. solution of ammonia till the washings are colourless; the filter is then dried at  $100^{\circ}$  and weighed. As the fibre is not quite pure, it is necessary in exact analyses to determine both ash and nitrogen in the fibre after weighing; the nitrogen is then calculated as albuminoids, and both albuminoids and ash are deducted from the crude fibre. In the case of substances containing fatty matters these should be removed with ether before commencing the determination of fibre. The reagents employed in this method dissolve the softer parts of both cellulose and lignose to a small extent. A trustworthy method of distinguishing between lignose and cellulose in the analysis of feeding materials is much to be desired, as the results of the German feeding experiments show that cellulose is digested by ruminants, while lignose is not. R. W.

**FORMIC ACID.**  $CH^O^2 = H.COOH$ . **Synthesis.**—This acid is produced by the union of hydrogen and carbon dioxide under the influence of the silent electric discharge:  $H^2 + CO^2 = CH^2O^2$ . When a stream of the mixed gases was passed

\* The feeding experiments conducted at Rugby by the Royal Commissioners with sewage and unsewaged grass, showed that an increase of nitrogen in the crop did not determine a greater feeding value if the conditions necessary for maturing the crop were absent. Thus late autumn sewage grass, though far more nitrogenous, was not equal in feeding value to the spring crops.

through a Siemens' induction-tube, a contraction of volume took place, the resultant gas was found to contain carbon monoxide, with a small quantity of marsh gas, and small drops of an oily liquid were deposited in the tube, which gave the characteristic reactions of formic acid (Brodie, *Proc. Roy. Soc.* xxi. 245).

On the Heat produced in the Formation and Decomposition of Formic Acid, see HEAT.

**Conversion of Formic Acid into Methyl Alcohol.**—Calcium formate, subjected to dry distillation, yields formic aldehyde, and this compound, treated with sodium-amalgam, yields a small quantity of methyl alcohol (Lieben a. Kossin, *Ann. Ch. Pharm.* cxviii. 107).

**Synthesis by means of Nascent Formic Acid.**—When ethylene gas is passed through a boiling aqueous solution of potassium cyanide and potassium hydrate (which yields formic acid), and the liquid afterwards distilled with sulphuric acid, an acid distillate is obtained, yielding a lead salt, only a small portion of which is soluble in water; and on distilling the soluble portion with sulphuric acid, boiling the distillate with mercuric oxide to remove formic acid, treating the product with sulphuretted hydrogen, and the filtrate with silver carbonate, a small quantity of a silver salt is obtained, having the characteristic acicular form of silver propionate. A similar result is obtained by passing ethylene gas through a mixture of oxalic acid and glycerin at 110–120°. It appears, then, that formic acid, in the nascent state, is capable of uniting with non-saturated hydrocarbons, yielding acids containing more carbon than the hydrocarbon employed (Carstanjen a. Schertel, *J. pr. Chem.* [2] iv. 51).

**FORMIC ALDEHYDE or FORMALDEHYDE,**  $\text{CH}_2\text{O} = \text{H} \cdot \text{CHO}$ . This compound is formed in small quantity, together with formic acid and marsh gas, by the action of the silent electric discharge on a mixture of hydrogen and carbon dioxide: the formation is represented by the equation:



It appears, also, to be produced in a similar manner from a mixture of hydrogen and carbon monoxide, the marsh-gas obtained in both reactions probably resulting from its decomposition:  $2\text{CH}_2\text{O} = \text{CO}_2 + \text{CH}_4$  (Brodie, *Proc. Roy. Soc.* xxii. 172).

Formaldehyde is also produced: a. By decomposition of methylal,  $\text{H} \cdot \text{CHO}(\text{CH}_3)_2$ , which is related to it in the same manner as acetal to acetic aldehyde. When a mixture of methylal and sulphuric acid is warmed, an odour of formaldehyde becomes perceptible, and a sublimate is formed consisting of the solid modification of formaldehyde. The action of cold sulphuric acid on methylal also gives rise to the liberation of formaldehyde, which, at the moment of its formation, combines with the sulphuric acid, forming a compound analogous to sulphate of chloral.

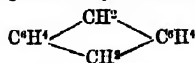
b. By the action of acids on methylene acetate, obtained by digesting methylene iodide with silver acetate and glacial acetic acid at 110°, and rectifying the distilled product over silver acetate. The portion boiling between 130° and 170° may be used either as such, or after being heated to 100° for six or eight hours with an equal weight of water. The latter liquid, which contains either free formaldehyde or the compound  $\text{CH}_2 = (\text{OH})(\text{OC}^2\text{H}^3\text{O})$  is called by Baeyer 'aqueous methylene acetate' (A. Baeyer, *Dent. Chem. Ges. Ber.* v. 1094; vi. 220).

**Action of Formaldehyde on Aromatic Hydrocarbons.**—Benzene treated with a mixture of methylal, acetic acid, and sulphuric acid, is converted into diphenyl-methane  $\text{CH}_2(\text{C}_6\text{H}_5)_2$ :



A mixture of 40 grams methylal, 120 benzene, and 400 glacial acetic acid is treated with a mixture of equal parts of glacial acetic acid and sulphuric acid till the greater part of the benzene has separated; the mixture after 24 hours is gradually mixed with 2,000 grams of sulphuric acid, keeping it cool; and the whole is left at rest for some hours, after which it is diluted with water and shaken up with ether. The ethereal solution when distilled yields diphenyl-methane.

Diphenyl-methane treated in a similar manner with methylal and acids is converted into a hydrocarbon,  $\text{C}^{14}\text{H}^{14}$ , which crystallises from alcohol in leaflets melting at about 90°, and having a constitution represented by the formula:



or else into the hydrocarbon  $\text{C}^{12}\text{H}^{12}$ , whose constitution is represented by the formula  $\text{C}^6\text{H}^5 - \text{CH}_2 - \text{C}^6\text{H}^5$ .

Formaldehyde and diphenyl yield a hydrocarbon which separates from chloroform in crystals.

When concentrated sulphuric acid is added to a mixture of methylene acetate, benzene and glacial acetic acid, an oil is formed which boils between  $260^{\circ}$  and a temperature above  $360^{\circ}$ , and consists of hydrocarbons.

Mesitylene, treated in a similar manner, gives a very characteristic reaction; by adding a cooled mixture of 10 parts acetic acid and an equal volume of sulphuric acid to a solution of 1 part mesitylene, 1 part methylene acetate, and 10 parts acetic acid, and leaving the mixture, after agitation from time to time, at rest for 24 hours, large colourless crystals are formed consisting of dimethyl-methane,  $\text{CH}_2(\text{C}_6\text{H}_4)_2$ , which by recrystallisation from ether, is obtained in monoclinic prisms having almost the form of cubes; they melt at  $130^{\circ}$  and resolidify at  $62^{\circ}$ . This body is so readily produced that its formation may be used as a test either of mesitylene or of formaldehyde. The reaction never fails, even if, instead of the pure aldehyde, a solution of methyl alcohol and chromic acid in glacial acetic acid is used (Bayer, *loc. cit.*)

*Action on Phenols.*—Aqueous methylene acetate and hydrochloric acid yield, with phenol, a colourless resin, with pyrogallol, a substance resembling tannin; and with resorcin, an insoluble body which burns like tinder. Gallic and salicylic acid form similar substances: the compound obtained with gallic acid forms colourless needles having the composition  $\text{C}^{12}\text{H}^{12}\text{O}^{10}$  (Bayer).

**FRANGULIN**,  $\text{C}^{20}\text{H}^{20}\text{O}^{10}$ , and **FRANGULIC ACID**,  $\text{C}^{11}\text{H}^{10}\text{O}^4$  (1st Suppl. 623). A. Faust (*Ann. Ch. Pharm.* clxv. 229), prepares frangulin by digesting the bark of *Rhamnus frangula* for three days with alcohol of 90 p.c. at  $25^{\circ}$ – $30^{\circ}$ ; partially distilling off the alcohol; adding lead acetate to the residue as long as a precipitate is formed; precipitating the filtered liquid with lead acetate; diffusing this precipitate through alcohol; and decomposing it with sulphuretted hydrogen. The resulting liquid filtered at the boiling heat yields, on cooling, crystals of frangulin.

Casselmann describes frangulin as crystallising under the microscope in square tables; Faust could not discern these tables either in his own preparation or in a specimen prepared by Casselmann; moreover, the two samples melted at  $226^{\circ}$  and  $225^{\circ}$  respectively, instead of  $243^{\circ}$ , as stated by Casselmann. Frangulin, after recrystallisation from hot alcohol, forms a lemon-yellow crystalline mass, and dissolves in alkalis with a deep cherry-red colour; when boiled with hydrochloric acid, it splits up into glucose and frangulic acid:



Frangulic acid, isomeric with alizarin, is most conveniently prepared by boiling the bark with rain-water for an hour, adding caustic soda, equal to one-twentieth or one-thirtieth of the weight of bark taken, and boiling again for several hours. The resulting liquid extract is supersaturated with hydrochloric acid, and boiled for some hours, whereupon the frangulic acid separates, and can be collected on a cloth filter; the dried and pulverised precipitate is boiled with alcohol, and the hot alcoholic solution precipitated by neutral lead acetate (which scarcely precipitates frangulic acid); the filtrate is precipitated with basic lead acetate; the precipitate disseminated through alcohol and decomposed by sulphuretted hydrogen; and the resulting liquid is heated to boiling and filtered hot, the acid then separating from the filtrate on cooling. This treatment with lead salts, &c., is repeated several times; and the purified acid, after being dried and boiled with benzene to separate sulphur, is finally recrystallised several times from hot alcohol. Different samples of bark differ much in the quantity of frangulic acid obtainable from them; in one case, 50 lbs. yielded only a few grams.

Frangulic acid melts at  $252^{\circ}$ – $254^{\circ}$ , and sublimes partially at lower temperatures: it is but little soluble in hot water, and insoluble in cold water and alum-solution; alkalis dissolve it, with a red colour, removed on boiling with zinc-dust; on treating it with red-hot zinc-dust, anthracene is produced in small quantities; it crystallises with  $1\frac{1}{2}$  mol. water, the last  $\frac{1}{2}\text{H}_2\text{O}$  being removed only at  $180^{\circ}$ .

*Dibromo-frangulic acid*,  $\text{C}^{11}\text{H}^8\text{Br}_2\text{O}^4$ , is obtained by adding bromine to an alcoholic solution of the acid; it is a light-red crystalline mass, difficultly soluble in cold alcohol.

*Diacetyl-frangulic acid*,  $\text{C}^{11}\text{H}^8(\text{C}^2\text{H}_3\text{O})_2\text{O}^4$ , is obtained by heating the acid with an excess of acetyl chloride in sealed tubes to  $130^{\circ}$ – $150^{\circ}$ ; it dissolves in about 300 parts of boiling alcohol, separating almost wholly on cooling, as a crystalline mass of four-sided prisms, visible under the microscope; it melts at  $184^{\circ}$ , and when decomposed by caustic potash-solution yields frangulic acid in its purest form.

**FREIESLEBENITE** (ii. 710). The crystalline system of this mineral has been variously stated to be monoclinic, rhombic, and triclinic. To decide this question, v. Zepharovich availed himself of the opportunity of examining a very fine crystal from Příbram, 2 mm. long,  $\frac{1}{2}$  m. broad, and terminated at one end with 22 exceedingly lustrous

faces, together with many other less perfect ones from the same locality. All his determinations accorded in indicating the rhombic system as the true one. The specific gravity of these crystals differing not inconsiderably from that of freieslebenite, v. Zepharovich examined the typical specimens of the latter from Freiberg and Hiendelaencina, and found them to agree, in respect to form and density, with the data given in Brooke and Miller's *Mineralogy*. The Příbram mineral, therefore, is not freieslebenite, as Reuss, from his analytical results, which undoubtedly correspond with the composition of freieslebenite, was led to believe.

v. Zepharovich arrived at the following conclusions:—

1. The mineral hitherto termed freieslebenite consists of two distinct species, the one monoclinic, the other rhombic.
2. The two species have the same composition, but differ in form and density.
3. The substance  $\text{Ag}^1\text{Pb}^2\text{Sb}^3\text{S}^{11}$  is, therefore, dimorphous.
4. The rhombic species, which has been termed diaphorite, and has a density = 5.90, is found at Příbram; no freieslebenite accompanies it. At Bräunsdorff, near Freiberg, it is also met with sparsely, and in association with freieslebenite.
5. The monoclinic species, freieslebenite, whose density is 6.35, appears most prominently at Freiberg and Hiendelaencina.
6. The forms of diaphorite and freieslebenite are allied by similar facial inclinations, and they in turn show a relation to the similarly constituted species, stephanite and antimonite (v. Zepharovich, *Jahrb. f. Mineralogie*, 1871, 277).

**FUCUSOL.** This substance, isomeric with furfural, obtained by boiling seaweeds with dilute sulphuric acid, has been re-examined by Stenhouse (*Proc. Roy. Soc.* xx, 80), who discovered it (ii, 718). The results of the new investigation agree perfectly with those of the former one as regards the differences in the physical properties of furfural and fucosol, the difference between the products obtained by the action of ammonia on the two substances, and between the bases derived from these products. *Fucosaniline hydrochloride* crystallises, like furfuraniline hydrochloride, in needles of a splendid purple colour.

Furfural, boiled with water and silver oxide, yields silver pyromucate,  $\text{C}^2\text{H}^3\text{AgO}^3$ , which crystallises in scales. Fucosol, similarly treated, yields an isomeric silver salt which is moderately soluble in boiling water, and crystallises, on cooling, in long flat needles.

*$\beta$ -Pyromucic acid*, separated from this salt by hydrochloric acid, crystallises from its aqueous solution in small rhomboidal plates melting at  $130^\circ$ , whereas ordinary pyromucic acid forms flat needles melting at  $133^\circ$  (Stenhouse), at  $134.3^\circ$  (Schwanert).

## G.

**GADOLINITE.** The bi-refracting crystals of gadolinite from Hitteröo, containing 10 to 12 p.c. of glucina, are monoclinic, having the axial ratio 1 : 0.848 : 0.630; angle of inclined axes =  $90^\circ 32'$ ;  $\infty P = 116^\circ$  (Descloizeaux, *Ann. Chim. Phys.* [4], xviii, 305); compare 1st *Suppl.* 627.

**GAHNITE**,  $\text{Al}^2\text{ZnO}^2$ , or  $\text{ZnO}.\text{Al}^2\text{O}^3$ . The specimens of this mineral found in the Franklin Furnace at Mine Hill, New Jersey, differ from the gahnite of other localities in the frequent occurrence of the cubic plane. These planes are often the largest, giving the crystals the form of cubes with truncated dodecahedral edges, and only small octohedral planes. There are also minute planes of the trapezohedron 202, truncating the edges of the dodecahedron; others of the trigonal-trisectahedron 30; and sometimes two planes between the cubic and octohedral which appear to belong to the forms 404 and 808. These surfaces, rounded and feebly lustrous, blend in a curved surface, and do not admit of accurate measurement. The inclinations on a cubic plane are: for 404,  $160^\circ 30'$ ; for 808,  $170^\circ 30'$ . The crystals vary in diameter from  $\frac{1}{8}$  to  $1\frac{1}{2}$  inch, are blackish green, their fragments being olive-green, and have a hardness = 7.5, and a specific gravity = 4.80–4.91. Two analyses gave as a mean result:—

Alumina . . . . .	49.78	Oxygen-ratios.	
Ferric oxide . . . . .	8.58	23.20)	25.77
Zinc oxide . . . . .	39.62	2.57)	
Manganous oxide . . . . .	1.13	7.82)	
Magnesia . . . . .	0.13	0.25)	8.12
Silica . . . . .	0.57	0.05)	
	99.81		

This gives the ratio of oxygen of R and H as 1 : 3.17. By assuming 1.56 p.c. of the ferric oxide to be present as the lower oxide, the ratio becomes exactly 1 to 3. This variety of gahnite is richer in zinc than any heretofore examined. It occurs in association with black mica, apatite, calcite, and a brownish variety of chrysolite which contains zinc (G. J. Brush, *Sill. Am. J.* [3], i. 28).

**GAIZE**, called also *Pierre morte*, is a siliceous rock underlying the cretaceous strata in the Department of the Ardennes, and forming in the southern part a layer 100 meters thick. It has a gray-blue to light brown colour; sp. gr. = 1.48. When gently ignited it loses 0.022 of its volume, and has then a specific gravity of 1.44. It may be cut with a knife. Crucibles made of it bear, without alteration, a temperature at which iron melts. It contains a large amount of soluble silica, and when boiled, after calcination, with caustic soda, yields a sodium silicate which, in the dry state, contains 68-69 p.c. of silica. The first eleven of the following analyses are by H. Sainte-Claire Deville & Desnoyers (*Compt. rend.* lxx. 581); the twelfth by A. Scheurer-Kestner (*ibid.* lxxii. 767).

	Silica		Alumina	Ferric Oxide	Lime	Magnesia	Water		Total
	Sol.	Insol.					Combined	Hygro-metric	
1. . . .	38.3	40.6	5.5	4.0	1.5	0.8	4.2	3.3	98.2
2. . . .	36.3	40.8	6.6	4.3	2.6	0.8	5.2	4.1	100.7
3. . . .	39.6	39.3	7.7	3.9	1.7	0.4	4.3	4.1	100.0
4. . . .	43.7	40.8	3.8	2.9	0.9	—	3.2	3.4	98.7
5. . . .	44.8	42.0	5.1	2.5	0.3	—	2.4	3.0	100.1
6. . . .	29.2	40.6	7.0	4.1	4.5	0.5	8.0	3.5	97.7
7. . . .	31.9	41.8	8.3	3.4	3.0	1.0	5.4	3.9	98.7
8. . . .	47.0	40.3	3.7	2.7	0.5	trace	2.3	2.7	99.2
9. . . .	39.2	39.0	3.8	2.0	4.1	1.0	7.2	2.9	99.2
10. . . .	30.0	24.7	5.2	2.5	9.5	1.6	23.5	3.4	100.4
11. . . .	46.2	38.4	4.5	3.1	trace	trace	3.9	4.2	100.6
12. . . .	43.7	40.8	3.8	2.9	0.9	—	3.2	3.4	98.7

**GALACTIN.** A nitrogenous substance obtained, according to Morin (*J. Pharm.* [4], xiv. 11), from milk by first precipitating the casein with acetic acid; coagulating the albumin by boiling; removing fat by ether; concentration; filtration from earthy phosphates; allowing the sugar to crystallise out; and finally precipitating the galactin by alcohol. As thus prepared it contains a little gelatin. 36 parts of dried milk yielded about 1 part of galactin.

Galactin is soluble in water, insoluble in ether and in alcohol, and is not transformed into gelatin by boiling its aqueous solution. It is precipitated by tannin, but the precipitate differs from the corresponding precipitate with gelatin in redissolving at a temperature of 60°. This property renders the detection of galactin in morbid fluids easy.

Galactin emulsifies fats. It is found in blood, gastric juice, animal membranes, milk, eggs, and many morbid animal fluids, and probably plays an important part in animal nutrition. It likewise exists in notable quantity in the juices of edible plants, and in the fluid of the embryonal cotyledons.

**GALBANUM OIL.** The blue oil obtained by distillation of galbanum appears, from Kachler's experiments, to be most probably identical with blue chamomile oil (p. 278).

**GALLEIN** and **GALLIN** (A. Baeyer, *Deut. Chem. Ges. Ber.* iv. 457, 565).—*Gallein*,  $C^{14}H^{14}O^4$ , is a colouring matter produced by heating pyrogallie acid with phthalic acid, or, better, with phthalic anhydride, for some hours, to 170°-200°, until the mass becomes thick; on dissolving it in hot alcohol, filtering, and adding water to



the filtrate, a precipitate of nearly pure gallein is obtained, which is easily purified by crystallisation from hot dilute alcohol. The crystals appear brown by reflected and blue by transmitted light; when the solution dries up, the gallein remains as a mass with a greenish-yellow metallic lustre. It is almost insoluble in cold water; in hot water it is sparingly soluble with a red colour; in alcohol it dissolves freely, forming a dark-red solution. Ether also takes up a little, but the solution is colourless. Gallein bears a strong resemblance to hæmatein, the colouring principle of logwood; like the latter, it dissolves in caustic potash with a splendid blue colour, the solution soon assuming a dirty tinge, and in ammonia with a violet colour. The colours which it produces on cloth mordanted with iron and alumina, are finer and more stable than logwood colours, and resemble more those of barwood.

Gallein is decomposed by heat like hæmatein, carbonisation taking place and no sublimate being formed. It is also converted by reducing agents into a colourless compound, gallin, just as hæmatein is converted into hæmatoxylin.

Gallein may also be formed by heating pyrogallie acid with trimetic, pyromellitic and prehnitic acids, as well as with phthalic acid. This shows that the phthalic acid takes no part in the reaction, which is simply a dehydration:  $3C^6H^4O^3 - 2H^2O = C^{18}H^{10}O^9$ . Other dehydrating agents, such as sulphuric acid and zinc chloride, yield on fusion with pyrogallie acid, brown or black bodies, but no gallein.

**Gallin,  $C^{18}H^{10}O^9$ .**—When gallein is boiled with a large quantity of water to which zinc and dilute sulphuric acid are added, the dark colour of the liquid changes to a light reddish-yellow, and on cooling, oily drops separate, which after some time become crystalline. These crystals consist of gallin rendered impure by gallein; the gallin is best purified by crystallisation from a warm aqueous solution of pyrogallie acid. It is obtained in beautiful glistening rhombohedrons and prisms, which are nearly colourless; dried *in vacuo*, they yield, on analysis, numbers agreeing with the formula above given. Gallin, in the solid state, or in aqueous solution, very readily assumes a red colour; it is less stable than hæmatoxylin, which in other respects it greatly resembles, being reoxidised to gallein in contact with ammonia, just as hæmatoxylin is converted into hæmatein. It dyes mordanted fabrics like gallein.

**GALLIC ACID,  $C^6H^4O^3$ .** This acid and pyrogallie acid are very easily oxidised by electrolysis. At first no oxygen is evolved at the positive pole, the gas being entirely absorbed; afterwards carbon dioxide is evolved, and eventually a mixture of this gas with oxygen and carbon monoxide (Bourgoin, *J. Pharm.* [4], xiii. 376).

**Derivatives of Gallie acid.**—In the preparation of ellagic acid by heating gallie acid to  $120^\circ$  with arsenic acid, if the product, insoluble in water and consisting chiefly of ellagic acid, be treated with sodium-amalgam, then acidified, filtered and agitated with ether, several substances are obtained which are distinguished from one another by the difference of their solubility in water.

Amongst them is a substance,  $C^{14}H^{10}O^7$ , consisting of pale greenish-yellow, glistening needles, which are sparingly soluble in cold water, and when treated with calcium hypochlorite, become first dirty violet, then brown, and finally almost colourless; with ferric chloride they become greenish-blue, then green, and on the addition of soda, greenish-brown; with ammonia they turn brown; with silver nitrate, brownish-black from reduced silver; and with nitric acid, yellowish. Strong sulphuric acid dissolves them partially, with yellow colour. Manganese dioxide and strong sulphuric acid give a fine purple-red.

The substance  $C^{14}H^{10}O^7$  is a weak acid, and the salts which it forms with the alkaline earths oxidise quickly in the air; a crystalline barium salt, however, appears to be formed by treating it with barium carbonate in a stream of hydrogen.

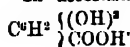
Occasionally, another crystalline substance, probably  $C^{12}H^8O^6$ , is obtained, which is also a weak acid, and but slightly soluble in water; it becomes red by treatment with ferric chloride. Amongst the products which are more soluble in water, and reddened litmus strongly, is found a substance which crystallises in plates, and gives a bluish-green reaction with ferric chloride (Rombold, *Ann. Ch. Pharm.* clvi. 116).

**Dibromogallie acid**, treated with silver oxide, yields carbonic and pyrogallie acids; heated with aniline, it yields gallie acid, together with pitchy products. Gallie acid is also produced on heating the dibrominated acid with argentocyanide of potassium (Priwoznik).

**Acetyl and Benzoyl Derivatives.**—By the action of acetyl chloride on gallie acid, Nachbaur has obtained a compound which he regards as tetracetyl-gallie acid (ii. 761). Schiff, however (*Ann. Ch. Pharm.* clxiii. 209), finds that, by the action of either acetic anhydride or acetyl chloride, a crystallisable product results, which yields 42.6 p.c. of acetyl on decomposition by magnesia, and is therefore triacetyl-gallie acid,  $C_{18}H_{10}O_9 \cdot 3(C_2H_3O)_2$ , which requires 43.5 p.c. acetyl, whereas the tetracetyl-acid would

require 51 p.c. Nachlaur also found that benzoyl chloride gave a dibenzoyl-acid; but Schiff finds that it is a tribenzoyl-compound. Neither the triacetyl- nor the tri-benzoyl-gallic acid gives any coloration with ferric chloride: hence no phenolic hydroxyl is present in these compounds.

In accordance with these results, Schiff assigns to gallic acid the formula

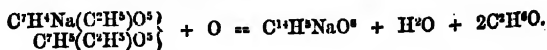


*Bromacetyl-gallic acid*,  $\text{C}^6\text{H}^2 \begin{Bmatrix} (\text{OH})^2 \\ \text{OC}^2\text{H}^2\text{BrO} \\ \text{COOH} \end{Bmatrix}$ , is formed by the action of gallic acid on bromacetyl bromide. It is an uncrystallisable compound, soluble in hot alcohol, and precipitable by water (Priwoznik, *Deut. Chem. Ges. Ber.* iii. 642).

*Tetracetyl-dibromogallic acid*,  $\text{C}^6\text{Br}^2 \begin{Bmatrix} (\text{OC}^2\text{H}^2\text{O})^2 \\ \text{COOC}^2\text{H}^2\text{O} \end{Bmatrix}$ , is formed, with evolution of hydrochloric acid, on dissolving dibromogallic acid in acetyl chloride. It is very slightly soluble in cold water, easily in boiling water, also in alcohol and in ether; crystallises in colourless needles which melt under water at  $91^\circ$  and decompose at a temperature a little above their melting-point. The aqueous solution gives, with ferric chloride, a violet colour quickly turning green (Priwoznik).

**GALLIC ETHERS** (Ernst a. Zwenger, *Ann. Ch. Pharm.* clix. 27). These ethers can be readily prepared by passing a current of dry hydrochloric acid through a boiling solution of gallic acid in anhydrous alcohol. When an excess of hydrochloric acid and of alcohol is employed, the acid is almost entirely converted into the ether. On evaporating the dark-coloured liquid to dryness at  $100^\circ$ , slowly heating the residue to its melting-point, and then crystallising the product two or three times from water, the ether is obtained in the pure state.

*Ethyl Gallate*,  $\text{C}^6\text{H}^2 \begin{Bmatrix} (\text{OH})^3 \\ \text{COOC}^2\text{H}^5 \end{Bmatrix} + 2\frac{1}{2}\text{H}^2\text{O}$ , crystallises from its aqueous solution in transparent rhombic prisms of a pale yellow colour, which melt in their water of crystallisation at  $90^\circ$ . It is scentless, and its solutions have a bitter taste and acid reaction. It is only slightly soluble in cold water, but dissolves easily in hot water, and crystallises out almost completely on cooling. It dissolves readily in alcohol and ether, and may be crystallised from chloroform—in which, however, it is but slightly soluble—in anhydrous colourless needles which melt at  $150^\circ$ . When cautiously heated, it sublimates in lustrous needles. Potassium and sodium hydrate decompose the ether in the cold, with liberation of alcohol; and if the air be permitted to have access to the solution, the alkaline gallate formed quickly oxidises, and assumes a dark colour. The ether gives precipitates with the salts of most of the heavy metals, but they have not been obtained of constant composition. The lead salt is a yellowish-white precipitate, the zinc salt a white, and the copper salt a reddish-brown precipitate. Ferrous salts colour the solution of the ether a pale violet, which changes to blue on exposure to the air, whilst ferric salts give the blue colour at once. Silver and gold salts are quickly reduced in the cold. The only compound of the ether which has been obtained of constant composition, was prepared by adding a slight excess of a cold saturated solution of acid sodium carbonate to a warm saturated solution of the ether. In a few minutes a compound having the formula  $\text{C}^6\text{H}^2\text{Na}(\text{C}^2\text{H}^3\text{O})^3 + \text{C}^6\text{H}^2(\text{C}^2\text{H}^3\text{O})^3$  separated in small, hard, yellow crystals. These were almost insoluble in cold water, but could with care be crystallised from hot water. The crystals are decomposed by hydrochloric acid, which removes the sodium and leaves pure gallic ether. When they are heated between two watch-glasses, the gallic ether sublimates, whilst the sodium ethyl gallate remains behind in a partially decomposed state. On heating a solution of the sodium-compound for some time, or better, a solution of the ether in an excess of sodium carbonate, a lemon-yellow crystalline precipitate is obtained, which is insoluble in cold water, but dissolves easily in solutions of the alkaline hydrates; the addition of hydrochloric acid to its alcoholic solution produces a pale yellow crystalline precipitate, which has the properties and composition of ellagic acid,  $\text{C}^{10}\text{H}^6\text{O}^8 + 2\text{H}^2\text{O}$ . The lemon-yellow powder is acid sodium ellagate,  $\text{C}^{10}\text{H}^2\text{NaO}^8 + \text{H}^2\text{O}$ , and is formed by oxidation of the sodium-compound of ethyl gallate:



Acid potassium carbonate has no action on the ether in the cold, but on applying heat, potassium ellagate is formed. When a solution of ethyl gallate in ammonia is exposed to the air, it first acquires a rose-red tinge which, after a time, becomes deep

red, and the solution finally deposits a greenish-yellow crystalline precipitate of ammonium colligate, which is scarcely soluble in ammonia.

According to Schiff (*Ann. Ch. Pharm.* cxliii. 209), an aqueous solution of ethyl gallate gives with excess of lead acetate, a precipitate having the composition  $Pb_2 \{C^2H^3(C^2H^3)O^3\}$ . This salt treated with ethyl iodide yielded much lead iodide but no definite organic product.

Ethyl gallate, boiled for some hours with acetyl chloride, forms ethyl triacetyl-gallate,  $C^2H^3(O.C^2H^3O)^3.COOC^2H^3$ . The oily product began to crystallise after eight months standing; it was insoluble in water, soluble in alcohol, gave no violet colour with ferrous salt, or precipitate with lead acetate (Schiff).

*Amyl Gallate*,  $C^6H^{12} \{ \frac{(OH)^3}{CO.O(C^2H^5)} \}$ , crystallises in fine, silky, colourless needles which melt at  $139^\circ$  and sublime when cautiously heated. It is scentless and has a bitter taste. It is slightly soluble in cold water, but more readily in hot water, the solution solidifying on cooling to a crystalline pulp. Its solutions have an acid reaction, and when the ether is heated under the surface of water, it melts to an oil. It is readily soluble in cold alcohol and ether, also in hot chloroform. No compound analogous to that obtained from ethyl gallate was observed on treating the ether with acid sodium carbonate, but its other reactions with alkalis and metallic salts are similar to those of the corresponding ethyl-compound (Ernst a. Zwenger).

#### GALLOTANNIC ACID. See TANNIC ACID.

**GALLS.** The following comparative analyses of English and Aleppo galls are given by J. Barrow (*Chem. News*, xix. 116).

	Aleppo	English
Tannin . . . . .	61.65	26.71
Gallie acid . . . . .	1.60	traces
Woody fibre . . . . .	15.68	47.88
Water . . . . .	12.32	20.61
Colouring matter, &c. . . . .	8.75	4.80
	100.00	100.00

**GARNET.** A transparent garnet occurs at Jordansmühl, in Silesia, partly implanted on decomposed prehnite; sp. gr. = 3.609. The crystals are dodecahedral, with their faces somewhat curved. The analysis was made with material somewhat contaminated with an imbedded chloritoid mineral, to which must be assigned a part of the oxides of manganese and nickel, the remainder constituting a nearly pure calcio-aluminic garnet:

$SiO^2$	$Al^2O^3$	CaO	FeO	MnO.	NiO	MgO	$H^2O$
37.88	21.13	31.28	4.19	0.15	0.18	2.88	1.08 = 99.07

(Websky, *Zeitschr. d. deutsch. geolog. Ges.* xxi. 753).

A green garnet from S. Piero in Elba has been analysed by G. vom Rath (*ibid.* xxii. 637, 660). It occurs, together with a massive reddish-brown garnet, and occasionally admixed epidote, in groups which are intimately united in their origin with a saussurite-gabbro. Sp. gr. = 3.286.

$SiO^2$	$Al^2O^3$	$Fe^2O^3$	CaO	MgO	N†
30.29	16.16	10.05	29.23	5.85	0.64 = 101.22

The *octohedral garnets* of the locality occur in a cleft of a nearly related rock, a mixture of garnet and epidote. Another locality, a short distance off, yields crystals of the combination  $\infty O . 2O_2$ , without any indication of O. The garnet of the granite vein of S. Piero shows either  $\infty O$  or  $2O_2$  predominant, sometimes with  $3O_2^3$  and  $\infty O_2$  subordinate. The colours are various, including shades of yellow, red, and green.

A light red garnet, sp. gr. 3.57, imbedded in a granular limestone from San Juan in Mexico, was found by Damour (*Compt. rend.* lxxiii. 1041) to contain:

$SiO^2$	$Al^2O^3$	$Fe^2O^3$	CaO	MgO	MnO	Loss by ignition
39.46	21.69	1.36	35.75	0.67	0.96	0.40 = 100.29

Small garnets, usually crystallised in dodecahedrons and easily detached from the rock, occur in a damourite slate in the neighbourhood of Salm-Château in Belgium. They belong to the variety known as *spessartin*, and contain 37 p.c. manganous oxide. This is somewhat remarkable in a crystallographic point of view, inasmuch as

\* Partly as FeO.

† Loss by ignition.

the so-called spessartin has hitherto been known only in the form of the trapezohedron 202, or of the combination 202 .  $\infty$ O (de Koninck, *Jahrbuch f. Mineralogie*, 1873, 319).

**Formation of Garnet from Chlorite.**—Pseudomorphs of chlorite after garnet have often been observed. One lately obtained from the Saualp in Carinthia, exhibits the half of a garnet-dodecahedron broken through the middle, and surrounded by a crust of chlorite about 4 mm. thick. The garnet has a columbo-red colour and fatty lustre; the chlorite is dark green with fine scaly structure. The thin laminae of chlorite appear to be deposited on the faces of the crystal very irregularly, and the surface of separation of the garnet and chlorite is irregularly zig-zagged. Under the microscope it is plainly seen that the chlorite has been formed from the garnet.

Analysis of the two minerals gave:

SiO <sup>2</sup>	AlPO <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	CaO	MgO	H <sup>2</sup> O	
38.59	17.57	16.43	21.12	2.27	4.27	—	= 100.25
25.19	21.66	9.09	14.92	—	18.73	11.53	= 100.12

To convert the garnet into chlorite, a third of the silica (13 p.c.), a third of the ferric oxide, a third of the ferrous oxide, and the whole of the lime have been removed, and at the same time 14 p.c. of magnesia and 11 p.c. water have been added (Niedzwiedki, *ibid.* 951).

**Conversion of Garnet into Mica.**—A case of pseudomorphosis of garnet into mica has been found in the mica crystals occurring in a vein of pegmatite at Roestoeel, near Arendal. As in another part of the same vein a great number of unchanged garnets are found, and the innermost part of some of the mica crystals consists of unchanged garnet, there can be no doubt that the mica crystals, which have the crystalline form of the garnet, owe their origin to a true pseudomorphosis. Comparing the experimentally determined composition of the unchanged garnets and of a mica crystal, it is found that the less soluble compounds, ferrous oxide, and the oxides of manganese, calcium, and magnesium, have been replaced by the more soluble oxides of potassium and sodium (A. Helland, *Pogg. Ann.* cxlvi. 480).

On the converse transformation of Mica into Garnet which accompanies the formation of Granulite from Gneiss, see GRANULITE.

**GAS ANALYSIS.** Frequent use is made in gas analysis of balls made of the dioxides of manganese or lead, or of lead phosphate, which, however, are extremely liable to break, especially after they have been soaked with phosphoric acid. To obviate this inconvenience, Ludwig (*Ann. Ch. Pharm.* clxii. 53) recommends mixing plaster of Paris with those absorption-agents which are not fusible, making the mixture into a paste with water, and pressing it round the platinum wire into the mould, the inside of which has been oiled. A hard ball, firmly attached to the platinum wire, is thus formed in a few minutes; but in order to prevent absorption of carbonic acid by the physical action of the pores, this ball has to be treated with phosphoric acid.

For the absorption of hydrogen sulphide, the balls are prepared by mixing two parts of lead phosphate with three parts of plaster of Paris. For the absorption of sulphur dioxide, balls consisting of plaster of Paris and dioxide of lead or manganese give good results.

For the determination of carbon monoxide, balls of plaster of Paris steeped in a mixture of one volume of saturated chromic acid solution and two volumes of water are left twelve hours in the mixture of gases to be examined. The carbonic acid formed has to be determined by absorption with potash.

The mould used for the preparation of the balls must in this case have its inside covered with a layer of paraffin, as oil would be acted upon by the chromic acid.

**Gas Analysis for Technical Purposes.**—C. Winckler (*J. pr. Chem.* [2], vi. 301) employs for technical gas analysis, an apparatus which is a modified form of Hoffmann's apparatus for the decomposition of ammonia, &c. It consists of a two-limbed tube, one limb of which is wider than the other, and furnished near the upper and lower ends with glass stopcocks, the space between these being graduated into fifths of cubic centimeters.

The second limb of the tube is connected with the first by means of caoutchouc tubing; it is also furnished with a stopcock (as in Hoffmann's apparatus). The apparatus may be turned upon its stand either vertically or horizontally, as required. The gas to be analysed is made to pass through the apparatus for some time, the stopcocks are then closed, and the volume of gas in the graduated tube is noted. The liquid which is to act as absorber is poured into the second tube, and by opening the lower stopcock of the graduated tube, some of it is made to pass into this latter.

To promote absorption, the apparatus is placed horizontally for a few minutes. After a little time the vertical position is resumed, and more liquid allowed to enter.

and so on, until on opening the connecting stopcock no further in-rush of liquid takes place. The level of the liquids in both tubes being made to coincide, the volume of liquid in the graduated tube corresponds with the volume of gas absorbed. If several constituents of a gas are to be estimated, a number of these instruments will be required.

To reduce the gas to a stated temperature, generally that of the absorbing liquid, it is made to pass through a small flask containing mercury, which is surrounded by a quantity of the liquid at the ordinary temperature of the air. The gases are usually passed through wetted cotton-wool before entering the graduated tube.

Water vapour is absorbed by strong sulphuric acid, carbon dioxide by caustic potash, and so on. A mixture of oxygen, carbon dioxide, sulphur dioxide, and nitrogen is analysed by absorbing the first three gases with pyrogallic acid in caustic potash; in another trial the oxygen and carbon dioxide are absorbed by caustic potash alone; and in a third, the sulphur dioxide only is removed by a solution of iodine in potassium iodide.

Carbon monoxide is absorbed by a solution of cuprous chloride in hydrochloric acid; if the gas contains at the same time carbon dioxide and oxygen, these are removed by bubbling it through tubes containing a solution of pyrogallic acid in caustic potash previous to its entering the apparatus.

The numbers given are generally within 0.1–0.3 p.c. of the theoretical amounts.

Another, and somewhat complicated, apparatus for technical gas analysis, especially for the determination of oxygen in the gases from the lead chambers, is described by Max Liebig (*Dingl. polyt. J.* cccvii. 37).

A simplified form of Frankland and Ward's apparatus for gas-analysis is described by J. Parry (*Chem. News*, xxiv. 282).

**GASES. Absorption by Charcoal.**—Experiments on the influence of pressure on the absorption of ammonia, carbon dioxide, and cyanogen gases by cocoa-nut charcoal have been made by J. Hunter (*Chem. Soc. J.* [2], ix. 76). Several series of observations were made on each gas. The results of those series which included the greatest range of pressure are given in the following table, in which V denotes the volume of gas absorbed by one volume of cocoa-nut charcoal at 6° C. and under the pressure P in millimeters.

Ammonia		Carbon Dioxide		Cyanogen	
V.	P.	V.	P.	V.	P.
170.7	760.0	73.2	760.0	107.5	760.0
174.3	1104.3	84.0	927.9	107.7	1160.6
176.0	1178.0	85.5	1014.6	110.3	1201.2
178.2	1269.2	87.3	1100.2	112.0	1628.8
180.8	1369.5	91.6	1412.8	115.4	1873.4
183.5	1486.5	95.5	1625.6	121.0	2204.7
188.7	1795.1	100.4	1912.9	124.9	2678.2
196.7	2002.6	108.0	2324.1		
209.8	2608.5	113.0	2960.2		
		132.4	3793.2		

These numbers show : 1. That the amount of absorption increases with the pressure. 2. That the same change of pressure produces about the same amount of increase in the quantity of each gas absorbed.

On comparing the relative weights of the absorbed gases, it is found that cocoa-nut charcoal absorbs a greater weight of cyanogen than of either ammonia or carbon dioxide.

**Influence of Temperature.**—Hunter has also made experiments on the influence of temperature on the quantity of ammonia and cyanogen absorbed by charcoal (*Chem. Soc. J.* [2], x. 649). Former experiments (1st Suppl. 630) had indicated that a gas capable of being largely absorbed by charcoal exists within the pores of that substance in a partially liquid state, and in accordance with this it is found that the volume of ammonia gas absorbed by cocoa-nut charcoal decreases regularly and continuously from 0° to 50°, but that at this point, beyond which probably the ammonia can no longer exist in the partially liquid state, a sudden change occurs, and from 50° to 80° the quantities of gas given off are considerably less for equal increments of temperature than between 0° and 50°. For cyanogen, on the other hand, the decrease of absorptibility is regular and continuous from 0° to 80°.

The following table exhibits the volumes, V., of the two gases (reduced to 760 mm.) absorbed by cocoa-nut charcoal at the temperatures, T., Centigrade :—

Ammonia		Cyanogen	
V.	T.	V.	T.
175.7	0°	113.7	0°
169.6	5	110.9	5
163.8	10	109.6	10
157.6	15	108.2	15
148.6	20	107.0	20
140.1	25	105.3	25
131.9	30	103.7	30
123.0	35	101.1	35
114.1	40	99.2	40
104.2	45	97.8	45
96.0	50	96.2	50
90.2	55	94.4	55
88.1	60	92.1	60
86.4	65	90.0	65
82.6	70	88.2	70
		86.7	75

The absorption of cyanogen is almost entirely confined to the first ten minutes, after which it proceeds much more slowly.

Hydrogen and nitrogen are but very slightly absorbed by cocoa-nut charcoal, one volume of the charcoal absorbing, on the average, 4.4 vol. hydrogen and 15.2 vol. nitrogen reduced to 3° C. and 760 mm.

**Diffusion of Gases.** J. Loschmidt (*Wien. Acad. Ber.* lxi. [2], 367; lxii. [2], 468; *Jahresb.*, 1870, 58) has made experiments on the free diffusion of gases, by means of an apparatus consisting of two glass tubes of equal length and diameter, closed at one end, and placed vertically one above another, the communication between them being closed or opened at pleasure by means of a sliding metal plate worked by a screw. The tubes were filled, first with mercury, then with the gases to be experimented upon, the apparatus placed vertically, the slider opened, shut again after half-an-hour to an hour, and the gaseous mixture analysed. In this manner, experiments were made with air and carbon dioxide; hydrogen and carbon dioxide; hydrogen and oxygen; carbon dioxide and oxygen; carbon dioxide and carbon monoxide; carbon dioxide and marsh gas; carbon dioxide and nitrogen monoxide; sulphur dioxide and hydrogen; carbon monoxide and oxygen; carbon monoxide and hydrogen;—at temperatures between -21° and +21°.

The diffusion-constant,  $K_1$ , calculated from the results of the experiments on these several mixtures, that is to say, the velocity with which the two gases mix, is approximately in inverse proportion to the square roots of the molecular weights, inasmuch as the values of  $K_1$ , calculated from the formula

$$K_1 = \frac{K_0}{\sqrt{m_1 m_2}}$$

come out very nearly equal. Perfect agreement is not to be expected, since the value of  $K_1$  is affected by the united influence of the volume and the form of the gaseous molecules, as well as by the nature of their constituent elements.

The diffusion-constant  $K$  is likewise proportional to the square of the absolute temperature, and with increased rarefaction, it is inversely proportional to the pressure of the gas,—so that

$$K = K_0 \frac{T^2}{p};$$

and by combining the expression  $K = \frac{K_1 T^2}{p \sqrt{m_1 m_2}}$  with that of Gay-Lussac and

Boyle's laws, according to the mechanical theory of gases, viz.:  $pv = \frac{mm^2}{2}$ , as well as

with that of the absolute temperature, viz.:  $T = \beta \frac{m m^2}{2}$ , we arrive at the remarkable formula,

$$K = l \frac{v_1 v_2}{N},$$

in which  $v_1, v_2$  denote the mean velocities of the molecules of the two gases,  $N$  the number of molecules in the unit of volume, and  $l$  a constant factor.

Wretschko (*Wien. Acad. Ber.* lxxii. [2], 575) has extended the preceding investigation to mixed gases. One of the tubes was filled with a gas A, the other with a gas B, and to both was added a third gas, C, in equal volumes p.c. The various gaseous mixtures were made with hydrogen, oxygen and carbon dioxide. A comparison of the resulting velocities of diffusion with those obtained by Loschmidt leads to the following conclusions:—

1. If the gas C is identical with either of the gases A, B, the diffusion-velocity of these gases is not altered by the admixture of C.

2. If C is different from both A and B, then—(a). The diffusion-velocity of A into B is altered by the admixture of C, to a greater degree in proportion as more of the gas C is present in each tube; and this velocity increases for the gases A and B when the gas C is specifically lighter than either; diminishes when C is specifically heavier than either; increases for the one gas and diminishes for the other when C, with regard to its sp. gr., lies between A and B;—(b). Whereas before diffusion there was an equal quantity of the gas in both tubes, this is no longer the case during diffusion, the specifically lighter of the two gases A and B being then found in larger proportion in the upper tube.

The preceding theorems relating to the diffusion, both of simple and mixed gases, have also been deduced by Stefan from the fundamental principles of the mechanical theory of gases (*Wien. Acad. Ber.* lxxiii. [2], 63-124), abstr. *Jahresb. f. Chem.* 1871, 51).

*Diffusion through Septa.*—Dufour (*Pogg. Ann.* cxlviii. 490) has made experiments on the diffusion of gases through porous walls, and the accompanying changes of temperature.

1. *Diffusion of Two Gases under Constant Pressure.*—On that side of the porous wall at which the gas diffuses inwards, there is an elevation of temperature, accompanied by a lowering of temperature at the other side. This is supposed to be due to a partial condensation of the gas on the porous substance in the one instance, and to a partial rarefaction in the other.

2. *Diffusion with Change of Pressure.*—When one gas diffuses into a porous vessel which already contains another gas (as hydrogen into a vessel containing air), there is a slight elevation of temperature, accompanied by an increase of pressure. As the first gas diffuses out, the thermometer falls until a point is reached at which it again begins to rise. Dry air diffuses into air which is relatively wetter than itself; this phenomenon is accompanied by the same changes of temperature as already noticed in the case of two gases.

*Thermo-diffusion.*—If a limited portion of a gas contained in an infinitely long tube were in a state of greater density than the rest, and it were heated unequally at both ends, a continuous motion of the gas would set in, which in the denser portion would be directed from the colder to the warmer end. This theoretical result, deduced by Neumann, has been verified experimentally by Feddersen (*Pogg. Ann.* cxlviii. 302), who obtained a greater density of the gas in one portion of a glass tube by introducing a plug of some gas-absorbing substance, as spongy platinum or palladium, plaster of Paris, charcoal, or magnesia alba.

In one case a plug of spongy platinum 31 mm. long was placed in a glass tube 12½ mm. wide, each end of which was connected with a narrower glass tube 3½ mm. wide; a drop of sulphuric acid placed in each of these tubes indicated the movement of the gas column as soon as both ends of the platinum plug were heated unequally. When, for instance, one end of the plug was heated to 200°, whilst the other one was kept as much as possible at 8°, the following results were obtained:—

Time				Cold side		Warm side	
				Observed	Calculated for 10' time	Observed	Calculated for 10' time
h.	m.	h.	m.				
12	0	until	12 16	225 mm.	225 mm.	no tube	—
12	10	"	12 15	94 "	188 "	95 mm.	190 mm.
11	15	"	12 25	no tube	—	241 "	241 "
12	25	"	12 30	105 mm.	210 "	95 "	190 "
12	30	"	12 35	110 "	220 "	no tube	—

As all the other substances gave similar results, it appears to be a general fact that porous substances used as diaphragms have the property of drawing gases through them from the cold towards the warm surface. Exactly the reverse of this phenomenon takes place in the diffusion of two different gases through a porous diaphragm, as a rise of temperature is observed on that side of the diaphragm where the gas with the greater power of diffusion enters.

**Endosmose of Gases through Vegetable Membranes.**—Barthélemy (*Compt. rend.* lxxvii. 427) has made experiments on the passage of gases through the leaf of a begonia, which by gradual withering during winter, had become reduced to mere cuticular tissue. When common air was dialysed through it, the gas passing through contained 31.41 p.c. of oxygen. The comparative permeability of the membrane to various gases was ascertained by exposing one surface of the membrane to the gas, and relieving the other side of pressure, the experiments being continued till equal volumes of gas had in every case passed, the different times required showing the relative permeability. It appears that the leaf membrane admits carbonic acid 13 to 15 times more readily than nitrogen, and 5 to 7 times more readily than oxygen. This high relative permeability of carbonic acid is somewhat diminished if the gas be quite dry. These results are similar to those obtained by Graham with a caoutchouc membrane.

**Mechanical Theory of Gases** (Naumann, *Ann. Ch. Pharm.* 1870, *Suppl.* vii. 340; *Deut. Chem. Ges. Ber.* ii. 690; Gmelin-Kraut's *Handbuch der Chemie*, i. Band, 1 ste Abtheilung, p. 14).

(1). *Relations between Volume, Pressure, and Temperature.*—According to the theory of Kröning and Clausius, explained in the article HEAT (iii. 131), the individual molecules of gases are supposed to be continually moving forward in straight lines, till they come in contact with other molecules or with the walls of the surrounding envelope, after which they rebound like elastic balls and recommence their rectilinear movement. The pressure of the gas may be regarded as the sum of all the impacts made by its molecules on the sides of the envelope, in consequence of their progressive motion. The pressure on a unit of surface will therefore depend: 1. On the mass of the individual gas-molecules; 2. On their velocity; 3. On the volume of the gas; 4. On the number of gas-molecules present.

Now let  $m$  and  $M$  denote the masses of two gas-molecules,  $c$  and  $C$  their velocities. The strength of the impacts of these molecules being directly proportional to their masses and to their velocities, will also be proportional to the products of these magnitudes, that is,  $mc : MC$ . But the number of impacts which take place in a given time is also proportional to the velocity: consequently, the pressures are proportional to the products of the masses of the molecules into the squares of their velocities:

$$p_{mc} : P_{MC} = mc^2 : MC^2 = \frac{mc^2}{2} : \frac{MC^2}{2}; \dots (1)$$

that is to say: *The pressure is proportional to the working force (vis vivâ) of the molecular movements.*

By the working force of the molecular movement of a gas we must here understand the mean working force of a molecule. For the several molecules, in consequence of their frequent collisions taking place in all imaginable directions, exhibit the most various changes of velocity, and at any given instant the most various amounts of working force,  $\frac{mc_1^2}{2}$ ,  $\frac{m^2}{2}$ ,  $\frac{mc_3^2}{2}$ , &c., the total amount of their working forces remaining, however, always the same. The pressure is therefore the same as if all the  $n$  molecules were actuated by the same working force, viz.:

$$\frac{mc^2}{2} = \frac{1}{n} \left( \frac{mc_1^2}{2} + \frac{mc_2^2}{2} + \frac{mc_3^2}{2} + \&c. \right)$$



Now let  $n$  be the number of gas-molecules at equal distances, and at rest, contained in a space whose cubical content is  $v$ . The unit of cubic space will then contain a number of molecules  $n_1 = \frac{n}{v}$ ; the number situated on a straight line equal to the unit of length will be  $\sqrt[3]{\frac{n}{v}}$ ; and the number in a square unit of surface will be  $\left(\sqrt[3]{\frac{n}{v}}\right)^2$ . Now in the state of motion the pressure on a square unit of surface must be proportional to the number of molecules which impinge upon that surface at equal times, *i.e.* directly proportional to the number of molecules in contact with it on any given instant, inasmuch as these molecules in their progressive motion come in contact with it at the same time. It is, moreover, directly proportional to the number of molecules situated on a unit of length, because the unit of surface will be struck more frequently in proportion as the distance between the molecules, or between the layers of molecules, is less. If the pressure corresponding with the volume  $v$  and number of molecules  $n$ , be denoted by  $p_{n1}$ , and the pressure corresponding with the volume  $V$  and number of molecules  $N$ , by  $P_{N1}$ , then—

$$\begin{aligned} p_{n1} : P_{N1} &= \left(\sqrt[3]{\frac{n}{v}}\right)^2 \sqrt[3]{\frac{n}{v}} : \left(\sqrt[3]{\frac{N}{V}}\right)^2 \sqrt[3]{\frac{N}{V}} \\ &= \frac{n}{v} : \frac{N}{V} = nV : Nv = n_1 : N_1 \quad . \quad . \quad (2) \end{aligned}$$

*i.e.* The pressures vary directly as the numbers of molecules and inversely as the volumes; or the pressures vary as the numbers of molecules in a unit of volume. This is Boyle's or Mariotte's law.

Since the relation of pressure  $p : P$  existing under given conditions is made up of the proportion  $p_{n1} : P_{N1}$  depending on the number of molecules in the unit of volume, and of the proportion  $p_{mc} : P_{MC}$  depending on the masses and velocities of the molecules, equations (1) and (2) give:

$$\begin{aligned} p : P &= \frac{p_{n1}}{P_{N1}} \cdot \frac{p_{mc}}{P_{MC}} = nV \frac{mc^2}{2} : Nv \frac{MC^2}{2} \\ &= n_1 \frac{mc^2}{2} : N_1 \frac{MC^2}{2} \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

*i.e.* The pressure exerted by a gas varies directly as the number and working force of the molecules, and inversely as the volume of the gas; or, as the number of molecules in the unit of space and the mean working force of the individual molecules.

This last equation follows also directly from the fundamental equation—

$$p = \frac{nmv^2}{3v} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

of which an elementary demonstration was given by Krönig under certain conditions which simplified the general problem (iii. 132), and a complete demonstration by Clausius (*Pogg. Ann.* c. 353), with the aid of the higher mathematical analysis. A complete demonstration of this important equation, requiring only the aid of elementary geometry and trigonometry, has lately been given by Pfaunder (*Pogg. Ann.* [1871], xlvii. 428); see also, Gmelin-Kraut's *Handbuch*, i. Abth. p. 18).

The relation between the pressure of a gas and the working force of its molecular movements, as given in equation (3), may also be represented by an expression depending only on the temperature. According to Gay-Lussac's law, established by experiment, the pressure of a perfect gas, whose volume remains constant, varies for each degree centigrade by  $\frac{1}{273}$  of the pressure which it exerts at 0°. If then,  $p_0, p_1, p_2$  be the pressure, answering to the temperatures  $t_0, t_1, t_2$ , we have:

$$\frac{p_1}{p_2} = \frac{p_0 + \frac{t_1}{273} p_0}{p_0 + \frac{t_2}{273} p_0} = \frac{273 + t_1}{273 + t_2} = \frac{T_1}{T_2} \quad . \quad (5)$$

$T_1$  and  $T_2$  denoting the temperatures reckoned from the absolute zero. Combining this with Boyle's law, according to which the pressure varies directly as the density,

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or as the number  $\frac{n}{v}$  of molecules contained in a given volume, we have :

$$p_1 : p_2 = \frac{n_1}{v_1} T_1 : \frac{n_2}{v_2} T_2 \quad . \quad . \quad (6)$$

*i.e. The pressures of equal volumes of any gas vary directly as the number of molecules in the unit of volume, and as the absolute temperatures.*

If, for the same gas,  $c_1$  and  $c_2$  denote the velocities of the molecules corresponding with the absolute temperatures  $T_1$  and  $T_2$ , equation (3) may be transformed into—

$$p_1 : p_2 = \frac{n_1}{c_1} \cdot \frac{mc_1^2}{2} : \frac{n_2}{c_2} \cdot \frac{mc_2^2}{2} \quad . \quad (7)$$

Consequently, from (6) and (7) :

$$\frac{mc_1^2}{2} : \frac{mc_2^2}{2} = T_1 : T_2 \quad . \quad . \quad (8)$$

*i.e. The working forces of the molecular movement of any given gas vary as the absolute temperatures.*

(2). *Equality of the Mean Working Force of Molecular Movement of Different Gases at the same Temperature.*—This proposition cannot be, or at least has not yet been, deduced from the fundamental properties of gases without the aid of the higher mathematics. Maxwell (*Phil. Mag.* [4], xix. 22) has shown that in a gaseous mixture, the molecules of all the component gases have the same working force of progressive motion; and an outline of his demonstration is given in Gmelin-Kraut's *Handbuch der Chemie* (p. 23). The main point consists in showing that, even supposing the working forces of molecular motion to have been different in the several gases composing the mixture, this difference would diminish at every impact between the molecules, and would actually in a very short time be reduced to nothing; that is to say, the several gases would all acquire the same working force of molecular motion. Now experiment shows that mixed gases diffuse in the same proportion as the constituents of the mixture when separate. Hence the molecular velocity, and therefore also the working force of molecular motion of the individual gases, cannot have been altered by the act of mixing. It follows, therefore, from Maxwell's theorem above cited, that before mixture also these several gases must, at the same temperature, have possessed equal working forces of molecular movement. Denoting, then, the molecular masses of two gases by  $m$  and  $M$ , and their velocities at the same absolute temperature by  $c$  and  $C$ , we have the equation :

$$\frac{mc^2}{2} = \frac{MC^2}{2} \quad . \quad . \quad . \quad (9)$$

If, then, in equation (8), which applies only to the same gas under different conditions, we substitute for  $mc_1^2$  its equivalent  $MC_1^2$  belonging to another gas, we have the equation :

$$\frac{\frac{1}{2}MC_1^2}{\frac{1}{2}mc_2^2} = \frac{T_1}{T_2} \quad . \quad . \quad . \quad (10)$$

*i.e. For different gases, also, the mean working forces of molecular movement are as the absolute temperatures.*

*Avogadro's Law.*—If in equation (3), page 545, representing the relation between pressure, number of molecules, volume, and working force of molecular movement, viz. :

$$\frac{p}{P} = \frac{nV \cdot \frac{1}{2}mc^2}{Nv \cdot \frac{1}{2}MC^2} \quad . \quad . \quad . \quad (11)$$

we substitute for the ratio of the working forces that of the absolute temperatures, namely,  $\frac{\frac{1}{2}mc^2}{\frac{1}{2}MC^2} = \frac{T_1}{T_2}$ , where  $T_1$  and  $T_2$  denote the absolute temperatures of the gases whose molecular masses are  $m$  and  $M$  respectively, we obtain

$$\frac{p}{P} = \frac{nVT_1}{NvT_2} = \frac{n_1T_1}{N_1T_2} \quad . \quad . \quad . \quad (12)$$

*i.e. The pressures of different gases are as the number of molecules and their absolute temperatures, and inversely as the volumes, or directly, as the number of molecules in the unit of volume and as the absolute temperatures.*

If now, in this last equation, we have

$$p = P, \quad T_1 = T, \quad v = V,$$

then

$$1 = \frac{n}{N}, \text{ and therefore } n = N. \quad (13)$$

i.e. At equal pressure and temperature, equal volumes of different gases contain equal numbers of molecules.

This is Avogadro's law, which is now regarded as affording the surest foundation for the determination of the atomic and molecular weights of all bodies which exist in or can be obtained in the gaseous state (see MOLECULE).

**Deviations from the Laws of Boyle and Gay-Lussac.** Researches on the influence of temperature on the deviations of gases from Boyle's law have been made by Amagat (*Compt. rend.* lxxii. 1170). Let  $p$  and  $p_1$  be the pressures corresponding with the volumes  $V$  and  $V_1$  at the temperature  $t$ ; also  $P$  ( $> p$ ) and  $P_1$  the pressures corresponding with the same volumes after the gas has been heated to  $T$ . Then, if the deviation depended only on the volume, we should have:

$$\frac{pV}{p_1V_1} = \frac{PV}{P_1V_1} \text{ i.e. } \frac{p}{p_1} = \frac{P}{P_1}.$$

The following table shows the mean values determined by experiment for sulphur dioxide, ammonia, and carbon dioxide:—

Name of Gas	Number of Experiments	$t$	$\frac{p}{p_1}$	$T$	$\frac{P}{P_1}$	Diff.
Sulphur dioxide	3	14°	0.50838	98°	0.50277	0.00561
Ammonia	2	13	0.50731	98	0.50402	0.00329
Carbon dioxide	3	13	0.50981	98	0.50771	0.00210

These numbers show that the deviation depends upon the temperature as well as upon the volume. Amagat explains this by supposing that with the greater working forces of the molecules at the higher temperature, the loss produced by their collision is proportionately less than the increase of pressure on the walls, in consequence of the increase of working force, notwithstanding the increased frequency of the collisions resulting from the higher velocity of the molecules.

Amagat has also determined the ratio  $\frac{pv}{p_1v_1}$  for several gases at different temperatures and under nearly equal initial terminal pressures, the volume being in each case reduced to nearly one-half.

Name of Gas	Temperature	Initial Pressure	$\frac{pv}{p_1v_1}$
		cm.	
Sulphur dioxide	15.3°	69.153	1.0188
	98.5	91.523	1.0078
	98.4	69.255	1.0057
" "	15.5	69.221	1.0182
	97.8	69.283	1.0051
	7.7	70.586	1.0125
Ammonia	98.0	70.500	1.0018
	6.1	70.210	1.0129
	98.5	92.382	1.0062
Carbon dioxide	98.4	70.354	1.0051
	8.5	71.537	1.0061
	98.1	71.053	1.0026
" "	9.0	72.055	1.0064
	98.4	72.100	1.0021
Air	7.2	72.560	1.0010
	98.4	72.512	1.0001
	97.5	71.458	0.9993

From these numbers it appears, that towards 100° sulphur dioxide and ammonia deviate but little from Boyle's law, though somewhat more than air at ordinary temperatures; that at 100° carbon dioxide deviates but very slightly from the law, a result in accordance with Regnault's determinations of the density of this gas; and that at 100° atmospheric air may be regarded as conforming exactly to Boyle's law.

In another series of experiments (*Compt. rend.* lxxiii. 183), Amagat has determined the values of  $\frac{pv}{p_1v_1}$  for sulphur dioxide and carbon dioxide, between the temperatures of 0° and 250°, the gases being originally under the atmospheric pressure, and then reduced to one-half of their volume; also the coefficient of expansion between the same limits of temperature.

Temperatures	Value of $\frac{pv}{p_1v_1}$		Expansion—Coefficient (air = 0.00367)	
	for SO <sup>2</sup>	for CO <sup>2</sup>	for SO <sup>2</sup>	for CO <sup>2</sup>
0°	—	—	—	0.003724
8	—	1.0065	—	—
Between 0 and 10	—	—	0.004233	—
„ 10 and 20	—	—	0.004005	—
15	1.0185	—	—	—
50	1.0110	1.0036	0.003846	0.003704
100	1.0054	1.0023	0.003757	0.003695
150	1.0032	1.0014	0.003718	0.003690
200	1.0021	1.0008	0.003695	0.003687
250	1.0016	1.0006	0.003685	0.003682

Hence it appears that, as the temperature rises, the deviation from Boyle's law and the coefficient of expansion both exhibit a regular decrease, the expansion-coefficient attaining its limiting value at the same temperature as that at which the gas begins to conform to Boyle's law.

Recknagel (*Pogg. Ann.* Ergänzungsband v. 563) has endeavoured to introduce into the law of tension of gases a precise mathematical expression of the influence of 'the neighbourhood of the condensation point,' and thereby so to generalize this law that it may represent the entire behaviour of the gas, including the phenomena which it exhibits in its passage to the liquid state. For carbon dioxide, with regard to the compressibility, increase of volume, and tension with temperature, and the tension and density of its saturated vapour, sufficient data have been furnished by the experiments of Regnault (*Mémoires de l'Académie des Sciences*, xxi. et xxvi.; *Jahresb.* 1847-48, 136; 1863, 88). The following results have been deduced:—

In place of the equation expressing the laws of Boyle and Gay-Lussac,  $Pv = A_0(1 + \alpha t)$ , there is obtained, for carbon dioxide and nitrogen monoxide, the equation:—

$$Pv = A_0(1 + \alpha t) \left(1 - \frac{B_t}{v}\right);$$

more general, and more exactly representing the results of observation, in which  $v$  denotes the volume of the unit of weight of carbon dioxide;  $B$  a function of the temperature determined by the tension of the vapour saturated at  $t^\circ$ ; and  $\alpha = 0.003612$ . If  $P$  is estimated in atmospheres, and the unit of volume is that which is occupied by 1 kilogram of carbon dioxide at 0°, and 1 atmosphere tension, then  $A_0 = 1.00710$ ;  $B^0 = 0.00705$ ;  $B_{100} = 0.0038$ ; and generally:

$$B^t = 1.00710(1 + \alpha t) \frac{1}{4M},$$

where  $M$  denotes the tension of the vapour saturated at  $t^\circ$ .

*Relations of Vapours to Boyle's and Gay-Lussac's Laws.*—H. Horwig (*Pogg. Ann.* cxxxvii. 19, 592) has made experiments on the relation between the pressure, volume, and absolute temperature ( $a + t$ ) in the vapours of alcohol, chloroform, carbon bisulphide, ether, and water. The apparatus used was so contrived as to admit of a simultaneous variation of the pressure, volume, and temperature of the vapour. A graduated glass tube, filled with mercury, into which the liquid to be volatilised was introduced in bulbs of thin glass, was connected at its lower end with a tube wider at the bottom

but gradually narrowing towards the top, which served as a receiver for the mercury driven out of the graduated tube by the pressure of the vapour, and communicated at its narrow end, by means of a T-tube, with an air-pump and a monometer. The graduated tube and the receiver were placed in a copper water-bath, in the sides of which were inserted plates of glass through which the two tubes could be viewed. The bulbs having been burst, the pressure and volume of the vapour were observed at a constant temperature from the point of saturation of the vapour to the point at which, at the same temperature, it began to follow Boyle's law, a condition indicated by the constancy of the products  $pv$ , which had previously been continually increasing.

Denoting by  $p_1$  and  $v_1$  the pressure and volume at a certain temperature of the vapour in its pure saturated state,—that is to say, when it has just taken up the last drop of liquid,—and by  $P, V$ , the pressure and volume for a state of the vapour in which, at the same temperature, it conforms to Boyle's law, it is found that for the vapours of alcohol, chloroform, carbon bisulphide, ether, and water, in the saturated state, the relation between pressure, volume, and temperature, is expressed by the equation—

$$\frac{PV}{T_1 v_1} = 0.0595 \sqrt{a + t}$$

instead of  $\frac{PV}{a + t} = \text{const.}$ , which is the relation for perfect gases. For the products

$pv$  lying between  $p_1 v_1$  and  $PV$ , no definite law of variation has yet been discovered.

The vapours of alcohol and chloroform, when not in contact with the liquids, begin to follow Boyle's law at the temperature  $9.5^\circ$ , the great difference of their maximum tensions appearing to have no influence on the position of this point.

The equality of the coefficient 0.0595 for five vapours so different in most respects to those above mentioned, renders it probable that this coefficient has likewise the same value for all other vapours. If this be the case, the amount of deviation of the pure saturated vapour from Boyle's law, at any given temperature, must be the same for all vapours.

*Mean Velocity of Molecular Movement for Imperfect Gases.*—Suppose a kilogram of a gas at  $0^\circ$  to be under an initial pressure so small that the volume  $v_0$  is extremely great, and consequently the attraction between the molecules may be regarded as nothing; and suppose that the pressure is increased to  $p'_0$ , whereby the volume is reduced to  $v'_0$ : then  $\frac{p_0 v_0}{p'_0 v'_0} = 1 + \Delta p$ , where  $\Delta p$  denotes the deviation from Boyle's law at the pressure  $p$ . If, now, while the pressure remains constant, the temperature be raised to  $t$ , and the volume  $v'_0$  thereby increased to  $v$ , we shall have:

$$\frac{v}{v'_0} = 1 + a_p t;$$

where  $a_p$  is the coefficient of expansion under constant pressure  $p$  between  $0^\circ$  and  $t^\circ$ . Assuming further:

$$\frac{p_0 v_0 a_0}{1 + \Delta p} = R_p; \text{ and } \frac{1}{a_p} = a_p,$$

we have:

$$pv = R_p (a_p + t),$$

where  $R_p$  and  $a_p$  vary with the pressure.

The values of  $R_p$  are as follow:—

	$p = 0$	0.76	1	5	10	15	20 met.
Air	$R_p = 29.222$	29.325	29.347	29.672	30.007	30.265	30.446
Carbon dioxide	$R_p = 19.239$	19.388	19.437	20.417	21.997	23.867	25.915

Now, according to Clausius (*Zamminer's Jahresh. f. Physik.* 1857, 36),

$$pv = \frac{u^2}{3g},$$

where  $g$  is the acceleration due to gravity, and  $u$  the mean velocity of the progressive motion of the molecules. Consequently,

$$u = \sqrt{3R_p (a_p + t)},$$

which formula differs from that of Clausius for perfect gases in this respect, that  $R_p$  and  $a_p$  are not constant, but functions of the pressure or volume.

For air and carbon dioxide observation has furnished the data required for calculating the following mean velocities in meters per second:—

Pressure in Meters	Air		Carbon Dioxide	
	$t = 4.8^{\circ}$	$t = 100$	$t = 3.3$	$t = 100^{\circ}$
0	485.1	566.0	393.3	459.7
0.76	484.4	566.9	392.1	459.2
1	484.8	566.9	391.8	459.0
5	483.8	566.9	385.0	456.4
10	482.8	566.9	374.5	452.8
15	482.0	566.9	362.9	449.4
20	481.4	566.9	350.4	446.2

The velocities found for the pressure 0 represent the ideal case of an infinitely expanded, that is, perfect gas, in which the molecular attractions are infinitely small (Blaserna, *Compt. rend.* lxxix. 134; *Jahresh. f. Chem.* 1869, 74).

**GASES, VOLCANIC.** The gases evolved from the solfataras of Vesuvius and the Campi Flegrei were examined by Deville in 1862 and by Fouqué in 1865. Goreix (*Compt. rend.* lxxv. 154) examined them in June 1869, collecting the gases as nearly as possible from the same points.

A small constant variation was observed in gas issuing from one and the same orifice, to such an extent that two consecutive analyses scarcely ever gave identical results; it was not probable, therefore, that any uniformity would be traceable in the gas from different centres of emanation, or that the present results would correspond closely with those of previous experimenters.

As a rule the gas evolved consisted mainly of carbon dioxide mixed with about 5 p.c. of hydrogen sulphides, less than 1 p.c. of oxygen, and from 5 to 10 p.c. of nitrogen: the percentage of the latter gas, however, varied greatly, sometimes increasing to the extent of 50 or 60 p.c. with a proportional decrease in the amount of carbon dioxide. In some instances small quantities of marsh-gas were detected.

At Lake Agnano, and at the *Grotta del Cane*, the gas which escaped was pure carbon dioxide; in the *Grotta d'Ammoniac* the hydrogen sulphide present in 1862 was no longer capable of being detected. At the *Grotta di Solf* the marsh-gas was mixed with a small quantity of hydrogen, but ethylene was absent, while the hydrogen sulphide, which had disappeared in 1865, was again present in notable proportions. At Castellamare this same gas had reappeared, and the proportion of carbon dioxide had considerably augmented.

On a subsequent occasion the following results were obtained:—

Source	CO <sub>2</sub>	H <sub>2</sub> S	O	N	Temperature
Great Solfatara . . . . .	88.8	7.0	0.7	4.5	110° to 120°
Stufa, E. . . . .	29.5	traces	13.2	57.3	25°
Lago d'Agnano . . . . .	96.1	—	—	—	—
Grotta del Cane . . . . .	77.0	—	—	—	—
Acqua ferrata del Pozello (Castellamare) . . . . .	29.1	00.0	0.7	70.2	Air, 28° Water, 25°

At Vesuvius aqueous vapours containing carbon dioxide, besides dry emanations of hydrochloric acid and sulphurous oxide, without carbon dioxide, at a temperature of 225°, were evolved from the crater and from fissures on the sides. From the great Solfatara there issued with much noise, a mixture of steam, hydrogen sulphide, carbon dioxide, and air. The sides of the cavity were covered with crystals of sulphur and sulphide of arsenic.

*Emanations from the Caldeira de Furnas, San Miguel, Azores:* in 1867.—Janssen and C. Sainte-Clare Deville examined the gases evolved by the Grande Caldeira of Furnas, and found them to consist wholly of carbon dioxide, sulphuretted hydrogen, and a trace of nitrogen, hydrogen and other combustible gases being absent. The recent experiments of Fouqué corroborate the above results. The residue left after treating 2,500 c.c. of the gas with potash was less than 1 c.c. and was incom-  
bustible.

It would seem, therefore, that the gaseous emanations of the Caldeiras differ materially in composition from those of the Geysers of Iceland, and from the Solfon of

Tuscany, since the latter invariably contain both hydrogen and carburetted hydrogen. They more closely resemble the solfataras of certain active volcanic districts (*Compt. rend.* lxxv. 1115).

*Gases evolved from the Volcanic Island of Santoria (Grecian Archipelago) after the Eruption of 1866.*—These gases have been analysed by Gorceix (*Compt. rend.* lxxv. 270-272), who found that, besides carbon dioxide, oxygen, and nitrogen, the proportions of which varied from day to day, and even from hour to hour (vide N in table), traces of hydrogen, sulphuric acid, and marsh-gas were detected. In April 1870, acid vapours (temp. about 115°), were still issuing at two points, the gas evolved having the following composition:—

Gas evolved on April 12, 1870.	Fumarole M	Fumarole N	
		Sample 1	Sample 2
Hydrochloric acid . . .	19.4	1.0	28.4
Sulphurous acid . . .	12.0	0.4	
Carbon dioxide . . .	68.5	98.5	
Oxygen . . .	nono	nono	14.0
Nitrogen . . .	nono	nono	57.3
	99.9	99.9	99.7

An analysis of the gas contained in the sea-water on the coast (date not stated) gave 25.5 p.c. CO<sub>2</sub>, 10.1 O, and 64.3 N.

*Gases evolved from the Volcano of Nisiro's* (Gorceix, *Compt. rend.* lxxvii. 597-601).—The gas collected during March 1873, from the fumaroles in the crater had the following composition:—

	<i>a</i>	<i>b</i>		<i>c</i>			<i>d</i>
Hydrogen sulphide . . .	65.0	74.0	77.0	74.0	71.7	70.0	8.6
Carbon dioxide . . .	30.0	21.6	18.0	21.6	24.0	25.3	90.2
Oxygen . . .	0.4	0.4	0.4	0.4	0.4	0.4	—
Residue . . .	4.6	4.0	4.6	3.7	3.9	3.8	1.2

*a* was from the older group of fumaroles: the residue was incombustible. *b* and *c* were from two apertures in the more recent group, the analyses being made at intervals of three days: the residue was combustible. *d* was from a solfatara in the island of Cos: the residue consisted of nitrogen.

The fumaroles are surrounded by deposits of sulphur, and the soil is impregnated with sulphuric acid.

**GASTRIC JUICE** (Kuhne, *Lehrbuch der physiologischen Chemie*). As the pepsin and hydrochloric acid of the gastric juice produce together effects on albuminous bodies which neither is capable of producing apart from the other, C. Schmidt has suggested that these substances unite to form a sort of conjugated acid, which he calls pepto-hydrochloric acid: that some such compound is formed is also rendered probable by the modification of the properties of the two substances which is seen in their mixture. Dilute hydrochloric acid, for instance, dissolves the calcareous salts out of bone, leaving behind the gelatinous matter, but gastric juice removes the gelatin and leaves a brittle mass consisting of the earthy salts. Pepsin, too, in a neutral solution is non-diffusible, but in the presence of dilute hydrochloric acid it dialyses readily.

The preparation of artificial gastric juice has been much simplified by Von Wittich's discovery that pepsin, its essential organic constituent, is soluble in glycerin. An active digestive fluid may be obtained by removing the mucous membrane from a fresh pig's stomach, except that portion near the pyloric orifice, cutting it into small pieces, placing them in alcohol for twenty-four hours, and then transferring into just sufficient glycerin to cover them; a little of the glycerin extract can be strained off when required, and a 0.1 p.c. solution of hydrochloric acid added to it. The hardening in alcohol before maceration in glycerin is not essential, but if it is omitted, the glycerin extract is very tenacious and difficult to strain, on account of its containing a large quantity of mucus. To obtain absolutely pure artificial gastric juice, pure pepsin must of course first be prepared, and then dissolved in the dilute acid (see Pepsin).

H. N. M.

**GEIERITE.** A mineral occurring at Wolfach in the Black Forest, in caespar or on antimonial silver, in crystals of the rhombic combination  $\infty P. mP\infty$ . It is silver-white, yields a sublimate of arsenic and sulphide of arsenic, and when heated on charcoal gives off arsenious oxide, sulphurous oxide, and vapour of antimony. Hardness = 5.5, sp. gr. = 6.550. The analysis, carried out by Petersen, leads approximately to the formula,  $FeS \cdot 5(Fe; Co)(As.Sb)$ :

S	As	Si	Fe	Co
5.18	62.29	4.37	24.33	4.40 = 100.57

The mineral also contains traces of manganese, zinc, nickel and lead (Sandberger, *Jahrbuch f. Mineralogie*, 1869, 315).

**GELSEMIUM.** The alcoholic extract of *Gelsemium sempervirens* yields, by evaporation, solution in water, acidulation, and agitation with ether, an acid which crystallises out in small quantity as the ether evaporates. This acid, called gelsemic acid, forms, after purification, colourless, scentless, and tasteless needles; unites with alkalis forming crystallisable salts; and dissolves in nitric acid with yellow or red colour becoming deep blood-red on addition of ammonia.

The alkaline solutions of the acid exhibit a yellow colour and blue fluorescence, to whatever degree they may be diluted. The acid sublimes at  $100^{\circ}$ .

The ethereal solution of gelsemium extract also contains an alkaloid, gelsemine, in larger quantity than the acid. This alkaloid, which may be extracted by addition of potash and agitation with chloroform, is, when purified, a white amorphous substance having an intensely bitter taste, slightly soluble in water, easily in chloroform, and in 25 pts. of ether; sulphuric acid dissolves it with red colour, changing to purple-red on heating. It melts below  $100^{\circ}$ . Alkalis precipitate it from the aqueous solutions of its salts; these salts also give precipitates with potassium dichromate, potassium sulphocyanate, picric acid, potassium iodide, hydrobromic acid, ferrieyanide and ferrocyanide of potassium, &c. It is very poisonous. (Wormley, *Americ. J. Pharm.*, 1870, 42.)

**GERANIUM OIL.** Indian geranium oil, as it occurs in commerce, exhibits considerable varieties of composition and properties. O. Jacobson (*Ann. Ch. Pharm.* clvii, 232) has examined two samples of it, both containing traces of copper, to which perhaps the greenish colour of the oil is due. One sample, of sp. gr. 0.887 at  $20^{\circ}$ , was found to be adulterated with about 8 p.c. of alcohol; the other, which was more viscid, and had a specific gravity of 0.910 at  $29^{\circ}$ , contained 20 p.c. of a fatty oil. The free acid, which was most abundant in the second oil, was separated by agitating the distillate obtained below  $210^{\circ}$  with potash-ley, and distilling the evaporated liquid with sulphuric acid; it proved to be valeric acid.

*Geraniol*,  $C^{10}H^{18}O$ .—This compound, isomeric with bornol, and with the essential constituents of the oils of eucypt, hops, coriander, and *Osmitopsis asteriscoides*, is obtained by repeated fractional distillation of the portion of the crude oil which passes over between  $210^{\circ}$  and  $240^{\circ}$ . It is a colourless, strongly refracting liquid, having a very fragrant smell of roses; not solidifying at  $15^{\circ}$ , and inactive to polarised light. It has a specific gravity of 0.8851 at  $15^{\circ}$  and 0.8813 at  $21^{\circ}$ , and boils at  $232^{\circ}$ – $233^{\circ}$ , that is to say, at a higher temperature than either of its isomerides. It is insoluble in water, but mixes in all proportions with alcohol and ether. On heating it with recently fused and pulverised calcium chloride to  $50^{\circ}$ , at most, filtering the liquid in dry air, and then cooling it slowly to  $10^{\circ}$ , a crystallised compound  $CaCl_2 \cdot C^{10}H^{18}O$  separates out, which is immediately decomposed at a higher temperature or by water.

Geraniol oxidises very slowly on exposure to the air, and then leaves on distillation a brown viscid mass, which is also left in variable quantities when crude geranium oil is distilled.

By dropping geraniol on melting potassium hydrate, potassium valerate is formed. Valeric acid is also produced in small quantity by prolonged boiling of geraniol with potash-ley or baryta-water. By oxidation with a cold, neutral solution of potassium permanganate, geraniol yields valeric acid together with fatty acids poorer in carbon, especially acetic acid, when the solution is allowed to become heated. With a hot solution of potassium chromate and sulphuric acid the principal product is acetic acid; valeric and succinic acids are also formed. Nitric acid produces nitrobenzene, hydrocyanic acid, oxalic acid, and a resin, but no analogue of camphoric acid.

*Geranyl chloride*,  $C^{10}H^{17}Cl$ , is formed by passing hydrochloric acid gas through geraniol, or by heating the latter to  $80^{\circ}$ – $90^{\circ}$  for several hours with strong aqueous hydrochloric acid. It is a yellowish, oily, optically inactive liquid, having a peculiar camphoraceous aromatic odour, a specific gravity of 1.020 at  $20^{\circ}$ , not solidifying at  $15^{\circ}$ ,



decomposed by distillation; silver nitrate in alcoholic solution precipitates the chlorine immediately and completely, even at ordinary temperatures.

*Geranyl bromide*,  $C^{10}H^{17}Br$ , and *Geranyl iodide*,  $C^{10}H^{17}I$ , are produced by decomposing the chloride in alcoholic solution at ordinary temperatures with bromide or iodide of potassium. The *cyanide* and *sulphocyanate* may be obtained in a similar manner by means of the corresponding potassium salts; also the *valerate*, *succinate*, and *benzoate*, which are fragrant oily liquids, not solidifying at  $-10^{\circ}$ , and not distillable without decomposition. The etherification may also be effected by heating geraniol to  $200^{\circ}$  for two hours with excess of cinnamic or benzoic acid, and washing with dilute solution of sodium carbonate.

*Geranyl oxide*,  $C^{10}H^{16}O$ , is produced by heating geranyl chloride with geraniol, or to  $180^{\circ}$ ,  $200^{\circ}$  with three or four times its bulk of water, or over the water-bath for same time with alcoholic potash. When purified by repeated distillation, it is a colourless liquid which floats on water, has a peculiar odour of peppermint, and boils at  $187^{\circ}$ – $190^{\circ}$ .

*Geranyl sulphide*,  $C^{10}H^{16}S$ , produced by treating the chloride with potassium sulphide in alcoholic solution, is a yellowish liquid, sinking in water and having a peculiar disagreeable odour. It unites with *mercuric chloride*, forming a compound insoluble in alcohol. When heated it gives off sulphurous oxide; and yields a distillate consisting chiefly of the terpene of geraniol.

The preceding reactions show that geraniol in its chemical relations, bears a great resemblance to borneol, and, like the latter, may be regarded as a monatomic alcohol,  $C^{10}H^{17}OH$ . The distinguishing physical characters, namely, that geraniol is liquid and has no action on polarised light, are repeated in almost all its derivatives.

*Geranene*,  $C^{10}H^{16}$ , is produced by distilling geraniol with phosphoric anhydride or zinc chloride. When purified by repeated rectification, finally over metallic sodium, it is a colourless, mobile, optically inactive liquid, having a specific gravity of 0.8225 at  $20^{\circ}$ , and vapour-density of 4.93 at  $237^{\circ}$ . In contact with the air it oxidises quickly, with abundant formation of ozone. It unites with *hydrochloric acid*, forming a liquid hydrochloride; does not appear to form a hydrate when treated by Wiggers' method for the preparation of terpin. With *nitric acid* it yields the same oxidation-products as the other terpenes.

**GEYSERS.** The valley of Furnas, in the eastern part of San Miguel, was disturbed about three centuries ago by volcanic eruptions, and the soil is now perforated by a number of geysers. The three largest and most active of these are called 'caldeiras.' Only one of these furnishes a continuous stream of water. Another sends forth intermittent currents; while the third emits only water-vapour and gas. Besides these boiling springs, there exist others which have a temperature of about  $16^{\circ}C$ . and whose waters are ferruginous. The water of some is very alkaline and but slightly sulphurous; others are not in the least sulphurous; many contain a considerable amount of hydroferrie carbonate and carbonic acid; and some, free sulphuric acid. These springs, especially those containing sulphuric acid, are used medicinally. All of them contain a large quantity of silica in solution, so large, indeed, that it is deposited at the mouth. Sodium salts and free carbonic acid are present in large quantity, while iron, lime, and magnesia are comparatively scarce. Several of the springs contain traces of bromides, iodides, and fluorides; boracic acid and arsenic are not present (T. du Fouqué, *Compt. rend.* lxxvi. 1361).

**GIRONA RESIN.** See RESINS.

**GLASS.** *Composition of various kinds.*—Crystalline glass from Dresden, easily fusible, and having a sp. gr. of 2.556 to 2.660, was found by H. Schwarz (*Dingl. pol. J.* civ. 423) to have the composition  $16SiO^2.2AlF^3.13RO$ , the symbol RO including manganese oxide, lime, magnesia, soda, and potash. Amorphous glass of sp. gr. 2.611–2.648, exhibited nearly the same composition, viz.:  $17SiO^2.2AlF^3.13RO$ . These glasses contain large proportions of manganese oxide (5.60–6.30), which acts like lead oxide, rendering them easily fusible. The manganese residues from chlorine works, such as the compound of manganese oxide and lime obtained in Weldon's process, might be usefully employed in their preparation. Venetian Mosaic glass, opaque and of light blue colour, was found by Schwarz to contain 5.92 p.c. antimonious oxide, 9.76 lead oxide and 1.32 copper oxide.

*Baryta glasses.*—Benrath (*Dingl. pol. J.* cii. 422) has endeavoured to determine how far baryta can be advantageously used as a substitute for the alkalis. Setting out on the supposition that no glass which does not approach more nearly to the composition of  $RO.3SiO^2$  than to  $RO.2SiO^2$ , can be of practical value, on account of its easy decomposability by water, &c., he has attempted to prepare glasses approaching the

former composition, in which more or less of the alkali has been replaced by baryta. A glass containing silica 58.48, baryta 30.56, potash 10.96—melted well—blew easily, had a medium hardness, and considerable lustre. As compared with a similar lime glass (*i.e.*, with an equivalent of lime in place of baryta), it was found to be of greater density and lustre, and more fusible; in resistance to chemical reagents it seemed to stand between lime and lead glass.

Attempts to increase the quantity of baryta in proportion to the other basic constituents, or to make the glass more acid, resulted in obtaining masses which became devitrified on cooling. Although glasses containing no alkali can be prepared from silica, lime, and baryta, they are practically infusible if they contain more silica than corresponds to  $\text{RO} \cdot 2\text{SiO}_2$ , and these are so easily decomposed as to be worthless.

It appears, then, that baryta can only be substituted for the lime, and not for the alkali of glass. See also Jenne (*ibid.* xciii. 259).

*Ancient Jewish Glass.* D. Campbell (*Chem. News*, xxiv. 283) examined a specimen of glass dug up in the neighbourhood of the Temple of Jerusalem at a depth of 20-80 feet. It was much weathered. Sp. gr. = 2.430. The least altered portions gave by analysis:

$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{SnO}_2$	$\text{PbO}$	$\text{P}_2\text{O}_5$
69.30	8.50	0.55	13.79	1.49	3.20	2.00	0.29	trace	0.80 = 99.92.

*Cryolite Glass. Milk Glass.*—Cryolite glass from the works of the American Hot-cast Porcelain Company, having a sp. gr. of 2.471, milk-white in the middle, opalescent to transparent on the outer and inner surfaces, and like ordinary good glass in the other parts, was found by Benrath (*Dingl. polyt. J.* xcvi. 237) to contain

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{CaO}$	$\text{Na}_2\text{O}$
67.07	10.99	1.02	1.09	trace	19.83 = 100.

Experiments in the glass furnace showed that a mixture of 1 part cryolite and 2 parts quartz-sand melted easily and became quite limpid, yielding a glass which remained transparent after rapid cooling, while at the bottom of the crucible, where the layer of glass was 5 mm. thick, the mass on cooling was completely converted into milk-glass. The glass, which was perfectly white, had a sp. gr. of 2.373, and gave by analysis 70.01 p.c.  $\text{SiO}_2$ , 10.78  $\text{Al}_2\text{O}_3$ , and 19.21  $\text{Na}_2\text{O}$ . Its formation may be represented by the equation:

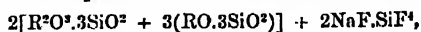


The silicon fluoride, which is evolved in large quantity (74 pounds from 300 pounds of the mixture), might be converted into silicofluoric acid available for the preparation of potassium salts, by simply connecting the covered melting pots with absorption-chambers containing water.

C. P. Williams (*Journal of the Franklin Institute*, lvii. 252) has made five analyses of cryolite glass, from which it appears to contain, on the average,

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{ZnO}$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	F
68.34	7.86	1.50	1.12	6.99	1.86	0.25	10.51	8.05.

The sum of these constituents must be diminished by 3.39 p.c. oxygen, equivalent to the fluorine. From this composition Williams calculates the formula:



and infers, from the proportion of soda, that the original mass consists of 67.19 silica, 23.84 cryolite, and 8.97 zinc oxide, but loses 39 p.c. of its fluorine as silicon fluoride by the melting process. He supposes that the sodium silicofluoride in cryolite glass acts in the same manner as the calcium phosphate in ordinary milk glass. Cryolite glass is peculiarly well adapted for coloration by metallic oxides. According to W. J. Cheyney, calcium fluoride may be substituted for cryolite in its preparation.

E. Richters (*Dingl. pol. J.* xciii. 259) has made experiments on the use of calcium fluoride, obtained in the preparation of carbonate of soda from cryolite, in glass making instead of lime. He finds that it leads to a considerable saving (nearly one-half) of Glauber's salt, without involving any increased consumption of fuel, or time of melting, or diminished yield; but that the iron contained in this artificial fluor-spar renders it unavailable for the preparation of white glass.

Sodium aluminate has been found to be more advantageous than cryolite for the preparation of milk-glass, as it does not attack the melting pots so strongly.  $1\frac{1}{2}$  cwt. of cryolite and  $\frac{1}{10}$  cwt. of calcined sodium carbonate is replaced by 1 cwt. of sodium aluminate. This preparation has also the advantage of containing less iron than cryolite (Stolba, *Dingl. pol. J.* xcvi. 178).

A very hard 'alabaster glass' examined by Stollé (*loc. cit.*) was found to contain

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	CaO	K <sup>2</sup> O	Na <sup>2</sup> O	
82.3	3.2	3.3	5.7	5.6	= 100.1.

The turbidity of this glass is probably due to the large proportion of silica, which induces a tendency to devitrification.

*Gold-ruby Glass.*—The conditions under which this glass is produced have been examined by W. Müller (*Dingl. pol. J. cci. 117*). Previous researches had shown that its formation does not depend upon the use of any particular preparation of gold, but that all the gold-compounds used in its production give up the gold in the metallic state at a temperature much below that required for the fusion of the glass. The quantity of gold taken up by the glass does not exceed a small fraction per cent. The auriferous glass may be either turbid or transparent, and in the latter case may exhibit various colours. Immediately after fusion the glass is colourless or yellowish, and the red, which is the tarnish-colour (*Anlaufarbe*), appears only when the solidified mass is heated to the temperature at which it begins to soften; this tarnish is independent of the atmosphere and of everything else by which the glass is surrounded. By actual fusion the glass again becomes colourless. The changes of colour in gold-glass are entirely owing to allotropic modifications of the gold; silicates of gold are unknown, and the assumption of their formation in the preparation of gold-glass is scarcely admissible. It still, however, remains to be determined in what manner the gold is taken up by the glass; also why the gold-glass turns red when heated, and not as the mass cools down from the fused state. The conditions of formation of the auriferous glass, and of its changes of colour, are also but very imperfectly determined. Müller's experiments have led to the following results:—

One hundred-thousandth part of gold is sufficient to give the glass a rose colour; the half of this amount has no perceptible effect. Glass containing lead takes up more gold than that which is free from lead; lead silicates may be made to take up  $\frac{1}{10000}$  of their weight of gold. The quantity of gold taken up affects the colour of the glass, but other circumstances influence it at the same time. Ordinary glasses, made by melting together lime, alkali and sand are not adapted for the preparation of gold-ruby. The addition of lead oxide has a very good effect on the colour of the ruby-glass, but it is limited by the inability of the melting pots to withstand the action of the lead oxide. Oxide of tin has no effect. An addition of *Vitrum antimonii* is said to make the colour less violet. To prepare an auriferous glass which shall take a good red colour, the temperature must be raised to the melting-point of cast-iron. If fused at a low temperature, the glass contains the gold in the separate state, and appears, not colourless, but yellow by reflected light, from the suspended gold-particles, and blue by transmitted light, exactly like a gold-solution from which the gold has been thrown down by ferrous sulphate. Gold-glass which reddens well can be obtained only by prolonged exposure to a high temperature for an hour and a half at the least. The melted glass will not take up gold if there is any 'glass-gall' floating on its surface. The addition of potassium sulphate or chloride to the glass immediately throws down the gold in spherules. Colourless gold-glass acquires the finest red colour when cooled as quickly as possible from fusion and then again heated. Sudden cooling leaves the glass colourless; slower cooling renders it turbid, part of the gold separating in granules, while that which remains in the glass does not impart to it the power of forming ruby-glass. Quenching the glass, that is pouring it into a large quantity of cold water, is especially resorted to in practice for producing a colourless glass capable of taking a good red colour. With regard to the colour of gold-glasses, those fluxes in which the gold is suspended in the glass must be distinguished from those in which it is really taken up or dissolved. The former may contain the gold as a black precipitate or a liver-brown mass according to the fineness of the suspended gold-particles. Those glasses in which the gold is taken up as a homogeneous constituent behave differently; and are colourless, yellow, or greenish-yellow before reheating, according to the quantity of the gold, the rapidity of cooling, &c.

The reddening of gold-glass takes place in various degrees. With good glass it begins at an incipient red heat, goes on quickly, and is completed by the time that the edges of the fragments begin to be rounded. In inferior glasses, the reddening takes place only at a higher temperature, when the glass begins to form drops, and sometimes so slowly that the glass must be repeatedly removed from the fire and reheated. The reddening succeeds better, in proportion to the quantity of gold taken up by the glass, the difference of temperature between the fused mass and the surrounding atmosphere, and the shortness of the time of cooling. It still remains to be explained why the same temperature acts differently on the auriferous glass accordingly as this temperature is attained by heating the glass, or by cooling it from the state of fusion.

In an appendix to Müller's paper, F. Knapp maintains that the gold in ruby-

glass is dissolved in the same manner as colouring matters are taken up by melted sugar and gelatin. Glass can also take up silver and copper in the same manner as gold. Colourless gold-glass is gradually reddened by light, even by diffused daylight, whence it appears that the allotropic modification of the gold may take place quite independently of the action of heat.

**Devitrification of Glass.**—Many kinds of glass when repeatedly heated become crystalline and more or less opaque. The change appears to be due to the crystallisation of silica, or of definite silicates rich in silica, previously held in solution in the amorphous glass, inasmuch as the amorphous portion is found to contain more alkali, while the crystallised or devitrified portion is richer in silica and lime. The addition of even a small quantity of sand to molten glass causes the formation of crystalline nodules, and when glass, towards the end of the melting, shows signs of crystallisation, the manufacturer knows that too much lime has been added. Glass is also especially apt to become crystalline when the crucibles are allowed to cool slowly. Henrivaux (*Bull. Soc. Chim.* [2], xix. 6) has analysed some of the crystalline nodules, and found that their composition is always different from that of the amorphous glass. Devitrified glass sweats in a damp atmosphere and gives up alkali to water (see *Chem. Soc. J.* [2], x. 387-386; xi. 244; xii. 543).

**GLAUCONITE.** A. Kupffer (*Jahresb. f. Chem.*, 1870, 1307) has analysed several Russian glauconites, of specific gravity 2.76-2.79:—1. From the Silurian limestone of the River Sibir, which forms the connection between Lakes Ladoga and Onega. 2. *a* and *b*. From the Silurian glauconite sand of Karyn-Oro near Ontika, Elisland. 3. From the Silurian limestone of the same locality: *a*, total analysis; *b*, after deduction of quartz. 4. From the Silurian limestone of Ballisehport, Elisland. 5. From the Silurian sandstone of the same. 6. From the tertiary sand of the green valley at Gadow:—

	SiO <sub>2</sub>	AlO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Quartz.	
(1).	49.42	10.23	16.01	3.00	3.78	0.31	7.91	0.26	8.05	0.80	= 99.80
(2) <i>a</i> .	52.00	9.63	15.89	4.36	3.94	0.12	7.81	0.22	5.38	0.48	= 99.83
(2) <i>b</i> .	51.93	9.20	15.31	4.73	3.79	0.30	8.02	0.20	5.52	0.40	= 99.40
(3) <i>a</i> .	41.57	9.92	10.90	2.49	3.19	0.08	6.09	0.26	6.65	18.84	= 99.99
(3) <i>b</i> .	51.24	12.22	13.44	3.06	3.93	0.10	7.50	0.31	8.20	—	= 100.00
(4).	50.91	9.81	16.54	4.80	3.62	0.30	8.09	0.14	6.48	—	= 100.69
(5).	52.38	10.53	13.77	4.36	4.96	0.08	8.00	0.04	5.88	—	= 100.00
(6).	49.76	8.18	16.00	3.77	3.97	0.41	7.57	0.52	9.82	—	= 100.00

**GLAUCOPYRITE.** A mineral from Guadalcanal in Andalusia, nearly related to the geleirite of Wolfach (p. 552). It occurs, together with fahl-ore, light red silver ore, and a small quantity of antimony-glance, in kidney-shaped masses composed of very thin scales. Twin and triple crystals also occur, formed on the type of coruscite; and apparently belonging to the rhombic combination  $\infty P_{\infty} \cdot \infty P_{\infty} P_{\infty}$ . Colour light lead-grey to tin-white, blackish at first, then acquiring a yellowish-brown and blue tarnish. Hardness = 4.5. Sp. gr. = 7.181. The analysis A, by R. Senfter, agrees approximately with the formula  $\text{FeS}^{12} \cdot 12(\text{Fe}; \text{Co}; \text{Cu}^2)(\text{As}; \text{Sb})$  which requires the numbers given in B:

	S	As	Sb	Fe	Co	Cu
A.	2.36	66.90	3.59	21.38	4.67	1.14 = 100.04
B.	2.47	69.45	—	28.08	—	— = 100

(F. Sandberger, *J. pr. Chem.* [2], i. 230).

**GLUCIC, or GLUCINIC ACID.** This acid, produced by the action of alkalis or acids on glucose (ii. 848), has been lately examined by H. Reichardt (*Vierteljahrsschrift pr. Pharm.* xix. 384, 503; *Jenaische Zeitschr.* v. 307), who assigns to it the composition  $\text{C}^{12}\text{H}^{22}\text{O}^{12}$ , or  $\text{C}^{12}\text{H}^{16}\text{O}^9 \cdot 3\text{H}^2\text{O}$ , whereas the earlier experiments of Peligot, Rochleder a. Kawaller, and Mulder (ii. 848), led to the formula  $\text{C}^{12}\text{H}^{16}\text{O}^9$ , analogous to those of the carbohydrates.

When dextroglucose is heated with baryta-water, a precipitate is formed consisting of the barium salt of saccharamic acid,  $\text{C}^{12}\text{H}^{16}\text{O}^{11}$ , and the liquid filtered therefrom contains the barium salt of glucic acid. On mixing this solution with basic lead acetate, filtering from the coloured precipitate at first produced, and again precipitating with basic lead acetate, lead gluconate is obtained; and on decomposing this salt with hydrogen sulphide and evaporating the filtrate at a gentle heat, glucic acid is obtained as a honey-yellow mass, which when dried over sulphuric acid, has the composition  $\text{C}^{12}\text{H}^{22}\text{O}^{12}$  + aq. or  $\text{C}^{12}\text{H}^{16}\text{O}^9 \cdot 3\text{H}^2\text{O}$  + aq. as further indicated by that of the lead-salt  $\text{C}^{12}\text{H}^{16}\text{O}^9 \cdot 3\text{PbO}$  or  $3\text{PbO} \cdot \text{C}^{12}\text{H}^{16}\text{O}^9$  thrown down from the neutralised solution of the acid by basic lead acetate, and dried at about 150°.

From a neutral or slightly alkaline solution of barium gluconate, alcohol throws down the tribasic salt  $3\text{BaO} \cdot 2\text{C}^{12}\text{H}^{16}\text{O}^9 + 6\text{H}^2\text{O}$ . An acid barium salt,  $\text{BaO} \cdot 2\text{C}^{12}\text{H}^{16}\text{O}^9 + 6\text{H}^2\text{O}$ ,

yellowish and very hygroscopic, is obtained by decomposing barium carbonate with glucic acid, and evaporating. The *acid calcium salt* is  $\text{CaO} \cdot 2\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 + 5\text{H}_2\text{O}$ . Magnesium carbonate is easily dissolved by glucic acid, and on evaporating the liquid a whitish-yellow easily friable mass is left, exhibiting when dried the composition  $\text{MgO} \cdot \text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 + 3\text{H}_2\text{O}$ . The *sodium salt*,  $3\text{Na}_2\text{O} \cdot 4\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 + 9\text{H}_2\text{O}$ , obtained by neutralisation, is hygroscopic and melts at  $100^\circ$ . The *aluminium salt*,  $\text{Al}_2\text{O}_3 \cdot 2\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 + 3\text{H}_2\text{O}$ , obtained by solution and evaporation, is, when dried at  $100^\circ$ , yellowish-white and somewhat hygroscopic. The *ferrous salt*,  $3\text{FeO} \cdot 2\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 + 6\text{H}_2\text{O}$ , obtained by decomposing the tribasic salt with ferrous sulphate, is hygroscopic after drying at  $100^\circ$ , and forms a green solution.

Glucic acid is easily decomposed, by heating its aqueous solution, into apoglucic acid (ii. 848), formic acid, and an acid said to be isomeric with acetic acid, most probably acetic acid itself.

Apoglucic acid has the composition  $\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4$  when dried at  $100^\circ$ , and  $\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4$  at  $140^\circ$ . From the composition of the lead salt,  $\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 \cdot \text{PbO}$ , or  $\text{PbO} \cdot \text{C}^{\text{H}}_2\text{H}^{\text{O}}_4$ , that of the acid dried at  $100^\circ$  is probably  $\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4 \cdot 3\text{H}_2\text{O}$  (H. Reichardt).

Since the acids, saccharic  $\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4$ , and glucic  $\text{C}^{\text{H}}_2\text{H}^{\text{O}}_4$ , formed as above, both contain a larger proportion of oxygen than the sugar from which they are formed, and as no oxygen is absorbed during the reaction, products containing less oxygen ought to be formed at the same time. Numerous experiments, however, have brought to light nothing of this kind, except acetone  $\text{C}^{\text{H}}_4\text{O}$ , or other volatile bodies of similar character (E. Reichardt. *Vierteljahrsschrift pr. Pharm.* xix. 516).

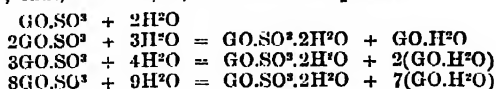
**GLUCINUM.** The atomicity of this metal is still a matter of doubt. Klatzo, in 1868 (*J. pr. Chem.* cvi. 227; *Jahresb.* 1868, 205) described a number of double sulphates, from the examination of which he concluded that glucinum sulphate is capable of crystallising with the sulphates of the magnesium metals (Mg, Fe, Mn, Zn, Cu) in all proportions, and in forms determined by the predominant basic constituent, whereas he did not succeed in obtaining double sulphates of glucinum with aluminic, ferric, chromic, or manganic sulphate: hence he inferred that glucina must be regarded as a monoxide,  $\text{GO}$ , belonging to the magnesium group. Marignac, on the other hand (*Ann. Chim. Phys.* [4], xxx. 45), was unable to obtain any of the double salts described by Klatzo. He finds that mixtures of solutions of glucinum sulphate and a magnesium sulphate invariably deposit the two salts in separate crystals, each of which may always be obtained pure if due care be taken to free it from adhering mother-liquor and from enclosed crystals of the other salts. The same want of success was experienced in attempting to form double nitrates of glucinum with the nitrates of magnesium, lanthanum, and didymium. Marignac also points out that the argument in favour of the diatomicity of glucinum, founded on the isomorphism of glucina and zinc oxide, has but little force, inasmuch as glucina might with equal reason be regarded as isomorphous with alumina, and that, in fact, there is but one well-established fact of isomorphism tending to show that the formula is  $\text{GO}$  rather than  $\text{GO}_2$ , namely, the isomorphism of phenakite,  $2\text{GO} \cdot \text{SiO}_2$ , and willemite,  $2\text{ZnO} \cdot \text{SiO}_2$ . On the other hand, the weakness of glucina as a base, and its great tendency to form basic salts, together with the frequent recurrence of the number 3 in the formulae of its salts, —e.g. in the hydrates  $3\text{GH}_2\text{O}_2 + 7\text{H}_2\text{O}_2$  and  $3\text{GH}_2\text{O}_2 + \text{H}_2\text{O}$ , the periodate  $3\text{GO} \cdot \text{IO}_3 + 11\text{H}_2\text{O}$ , and in solio-glucinic sulphate  $3\text{GSO}_4 \cdot 2\text{Na}_2\text{SO}_4 + 12\text{H}_2\text{O}$ , —may be cited as arguments in favour of its triatomicity. On the whole, then, the question remains much in the same state as it was several years ago (compare ii. 849), and is likely to remain so, until we obtain a satisfactory determination of the vapour-density of glucinum chloride, or of the specific heat of the metal.

Elaborate investigations of the salts of glucinum have lately been published by Atterberg (*Bull. Soc. Chim.* [2], xix. 497; *Kongl. Vetenskaps. Akad. Handlingar*, Bd. 12; *Deut. Chem. Ges. Ber.* vii. 472). He finds that the composition of the basic salts is very variable. In addition to the easily-obtained bibasic salts, glucinum forms also tribasic and 7–8 basic up to 13–14 basic salts. Experiments on the precipitability or non-precipitability of different acids by solutions of bi- and tri-basic glucinum salts, have led to the following classification of acids with regard to their chemical relations to glucinum:—

1. Neutral salts, and likewise bi- and tri-basic salts, soluble: *hydrochloric, hydrobromic, hydriodic, sulphocyanic, nitric, chromic, perchloric, formic, and acetic acids.*
2. Neutral and bibasic salts, soluble; tribasic (insoluble or) decomposed by cold water: *sulphuric, selenic, iodic, oxalic, hydroferrihydric, tartaric, and citric acids.*
3. Neutral salts, soluble; bibasic, insoluble: *selenious, succinic, hydroferrocyanic, hydrofluoric, and hydrofluosilicic acids.*
4. Neutral salts, insoluble and easily prepared: *periodic, phosphoric, and benzoic acids.*

With regard to the rational constitution of the basic salts, an important point

established by Atterberg's experiments is that, when dried at 100°, they contain a quantity of water corresponding with the quantity of neutral salt and with the excess of oxide present; thus, in the 2-, 3-, and 8- basic sulphates:—



Hence Atterberg infers that the basic salts of glucinum (and probably, also, other basic salts) must be regarded as molecular compounds of the neutral salt and the hydrate.

**Chlorides.**—In addition to the neutral chloride,  $\text{GCl}^2 + 4\text{H}^2\text{O}$ , glucinum forms several basic chlorides or oxychlorides: e.g.  $3\text{GCl}^2.2\text{GH}^2\text{O}^2$ ;  $\text{GCl}^2.3\text{GH}^2\text{O}^2$ ; these, however, are definite only in solution, the former in dilute, the latter in concentrated solution. It also forms the insoluble oxychloride  $\text{GCl}^2.12\text{GH}^2\text{O}^2 + 10\text{H}^2\text{O}$ , and double salts with auric, mercuric, and stannic chloride (Atterberg).

The **platinochloride**,  $\text{GCl}^2.\text{PtCl}^4$ , prepared by dissolving glucinum hydrate in solution of platonic chloride, is very readily soluble in water, and separates from a hot concentrated solution as an orange-coloured crystalline powder. By slow evaporation it crystallises in short four- or six-sided prisms, with angles of 90° and 135°. Crystallised under the microscope, it forms four-, six-, or eight-sided tables, with the same angles, sometimes, also, octohedrons apparently belonging to the quadratic system.

These crystals have the composition  $\text{GCl}^2.\text{PtCl}^4 + 9\text{H}^2\text{O}$ . Crystallised glucinum platino-chloride does not therefore correspond, either in composition or in crystalline form, with the magnesium salts  $\text{MgCl}^2.\text{PtCl}^4 + 6\text{H}^2\text{O}$  and  $\text{MgCl}^2.\text{PtCl}^4 + 12\text{H}^2\text{O}$ , but it agrees in composition with the calcium salt  $\text{CaCl}^2.\text{PtCl}^4 + 9\text{H}^2\text{O}$ ; this last salt does not crystallise well, so that its form is not distinctly known. The crystallised glucinum salt gives off 5 mol. water at 120°, and may then be heated to 200° without further loss. The dried salt,  $\text{GCl}^2.\text{PtCl}^4 + 4\text{H}^2\text{O}$ , is analogous in composition to the barium salt (J. Thomsen, *Ann. Ch. Pharm.* clvii. 363).

**Double Fluorides.**—**Potassio-glucinic fluoride** was described by Berzelius (ii. 832) and afterwards by Awdejew (*Pogg. Ann.* lvi. 101). Klatzo, on the other hand (*loc. cit.*), did not succeed in preparing either this or the corresponding sodium salt. According to Marignac, however (*Ann. Chim. Phys.* [4], xxx. 45), they are easily obtained by concentrating the mixed solutions of glucinum fluoride and potassium or sodium fluoride, and may be recrystallised from water. The **potassium salt**,  $2\text{KF.GF}^2$ , generally forms hard mammellated crusts, but by cooling a somewhat dilute solution, it may be obtained in crystals derived from a right rhomboidal prism. They generally present the form of thin hexagonal plates, the basal planes being largely developed. When the solution contains excess of potassium fluoride, the crystals have the appearance of rectangular prisms, owing to the elongation of one of the secondary axes. The salt is soluble in 19 parts of boiling water or in 50 parts at 20°. When heated it decrepitates and melts at a low red heat: it contains no water. By concentrating a solution containing a large excess of glucinum fluoride, a second salt,  $\text{KF.GF}^2$ , was obtained, forming a hard, vitreous, mammellated crust, from which no determinable crystals could be extracted; neither could it be recrystallised from water.

**Sodio-glucinic Fluorides.**—The compound  $2\text{NaF.GF}^2$  crystallises in two forms, one derived from a right and the other from an oblique rhomboidal prism. It is soluble in 34 parts of boiling water, or in 68 parts at 18°. After fusion at a red heat, it solidifies to a transparent glass, which falls to powder spontaneously. The compound  $\text{NaF.GF}^2$  is very similar to the potassium salt.

The **ammonium salt**,  $2\text{NH}^4\text{F.GF}^2$ , forms prismatic crystals isomorphous with the potassium salt.

**Cyanide of Glucinum** appears to be capable of existing only in very dilute solution; barium cyanide, decomposed by glucinum sulphate, gives a solution containing traces only of glucinum cyanide. The **platinocyanide**,  $\text{GCy}^2.\text{PtCy}^2$ , is obtained by decomposing barium platinocyanide with glucinum sulphate, and purified by solution in alcohol and ether. Below 30° it contains water and is golden yellow; at 80° it becomes orange-coloured; at a higher temperature it appears red and green. **Glucinum-magnesium platinocyanide**,  $\text{GMG}^2.\text{Pt}^2\text{Cy}^{12} + 16\text{H}^2\text{O}$ , crystallises from a mixture of magnesium and glucinum platinocyanides, in colourless crystals. At the same time other double compounds, which are dichroic, are produced (Toczynski, *Zeitschr. f. Chem.* [2], vii. 275).

**Ferrocyanide.**—Glucinum sulphate is not precipitated by potassium ferrocyanide, and on heating the liquid, Prussian blue separates out; a basic ferrocyanide is, however, obtained on addition of ammonia (Toczynski)

*Oxygen-compounds of Glucinum* (Atterberg, *loc. cit.*).—The hydrate recently precipitated by ammonia has the composition  $3(\text{H}^{12}\text{O}^2 + 7\text{H}^2\text{O})$ , and, after drying at  $100^\circ$ ,  $\text{GH}^2\text{O}^2$ ; from a boiling solution of glucina in potash it is precipitated as a compact powder containing  $3\text{GH}^2\text{O}^2 + \text{H}^2\text{O}$ .

*Sulphates*.—The normal salt  $\text{GSO}^4 + 4\text{H}^2\text{O}$ , gives off 2 mol. water at  $100^\circ$ , the third at  $150^\circ$ , the fourth at a higher temperature, and the whole of its acid when exposed to a prolonged red heat. It does not crystallise as a double sulphate with ferrous or cupric sulphate. Marignac describes a hex-hydrated sulphate obtained accidentally, in foliated prismatic crystals, which were very efflorescent and lost their brilliancy on removal from the mother-liquor.

*Basic sulphates*.—The salt  $\text{GSO}^4.\text{GO}^2\text{H}^2 + 2\text{H}^2\text{O}$  is formed by dissolving glucinum hydrate or carbonate in a solution of the neutral sulphate. It is a transparent, amorphous mass, which, when dried at  $100^\circ$ , has the above composition. At  $200^\circ$  it loses two mols. of water.

$\text{GSO}^4.5\text{GO}^2\text{H}^2 + 2\text{H}^2\text{O}$  is produced when the solution in which it is formed is boiled.

*Potassio-glucinic sulphates*.— $\text{K}^2\text{G}(\text{SO}^4)^2 + 2\text{H}^2\text{O}$ , is a white crystalline powder, slightly soluble in cold water, easily soluble in warm water.

$\text{K}^2\text{G}(\text{SO}^4)^2.2\text{KHSO}^4 + 4\text{H}^2\text{O}$  is precipitated on adding sulphuric acid to a mixed solution of the two sulphates. It gives off  $4\text{H}^2\text{O}$  at  $100^\circ$ .

*Sodio-glucinic sulphate*,  $2\text{Na}^2\text{SO}^4.3\text{GSO}^4 + 12\text{H}^2\text{O}$ , forms needles grouped in stars, unalterable in the air, and giving off  $7\text{H}^2\text{O}$  at  $100^\circ$ .

*Ammonio-glucinic sulphate*,  $(\text{NH}^4)^2\text{SO}^4.\text{GSO}^4 + 2\text{H}^2\text{O}$ , gives off two mol. water at  $110^\circ$ .

*Sulphite*.—When a solution of glucina in saturated aqueous sulphurous acid is evaporated, part of the acid escapes, and a viscous basic salt is obtained, probably having the composition  $(\text{GSO}^2.\text{GO}^2\text{H}^2 + 2\text{H}^2\text{O})$ .

The *hyposulphate* cannot be crystallised; its solution, when evaporated, evolves sulphurous acid.

*Selenate*,  $\text{GSeO}^4 + 4\text{H}^2\text{O}$ .—A very soluble salt which loses  $2\text{H}^2\text{O}$  at  $100^\circ$ .

*Selenite*. A solution of glucina in selenious acid does not yield crystals by evaporation; but ammonia gives a white flaky precipitate of  $2\text{GSeO}^2.\text{GO}^2\text{H}^2 + 5\text{H}^2\text{O}$ , which loses  $3\text{H}^2\text{O}$  at  $100^\circ$ .

*Chromate*.—A solution of glucina in chromic acid does not yield crystals by evaporation. The addition of neutral potassium chromate to a solution of glucinum sulphate precipitates a basic salt, which is decomposed by washing with water.

*Molybdate*,  $\text{GMO}^4.\text{GO}^2\text{H}^2 + 2\text{H}^2\text{O}$ .—Obtained in fine needles, almost insoluble, by prolonged ebullition of glucinum hydrate with molybdic acid.

The neutral *nitrate* is decomposed, on evaporation, with formation of a basic salt. The *chlorate* is still more easily decomposed, with evolution of chlorine. The *perchlorate*,  $\text{GClO}^4 + 4\text{H}^2\text{O}$ , forms needle-shaped, deliquescent crystals. The *periodate*,  $3\text{GO}^2.\text{I}^2\text{O}^2 + 13\text{H}^2\text{O}$ , is nearly insoluble in pure water.

The *orthophosphate*,  $\text{G}^3\text{P}^2\text{O}^8 + 7\text{H}^2\text{O}$ , is precipitated on adding ordinary disodic phosphate to a solution of neutral glucinum sulphate.

Two basic *oxalates* have been obtained, one soluble, the other insoluble. The *neutral oxalate*, as well as the *succinate* and *tartrate*, crystallises with difficulty from a syrupy solution (Atterberg).

*Potassio-glucinic Tartrates*.—A solution of 2 mol. cream of tartar and 1 mol. glucinum hydrate deposits, on evaporation, first cream of tartar, and then the double salt  $\text{C}^4\text{H}^2\text{K}^2\text{GO}^4$ , in peculiar crystalline growths somewhat resembling yeast-cells. Another salt,  $\text{C}^4\text{H}^2\text{K}^2\text{G}^2\text{O}^4 + 3\text{H}^2\text{O}$ , is produced by boiling cream of tartar with excess of glucina (Toczynski, *loc. cit.*).

Double tartrates of glucinum and antimony are obtained as non-crystalline substances, by boiling together antimonious oxide, glucina, and tartaric acid (Toczynski).

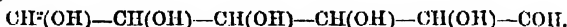
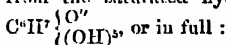
**GLUCONIC ACID**,  $\text{C}^6\text{H}^{12}\text{O}^7$ . (Hlasiwetz u. Habermann, *Ann. Ch. Pharm.* clv. 120.) An acid produced by the oxidising action of chlorino-water on glucose or cane-sugar. A dilute solution of the sugar is treated with chlorino-gas as long as absorption takes place, the process going on for four or five days when a considerable quantity of the sugar-solution is employed. The chlorine is then expelled by a stream of carbonic anhydride; the liquid is warmed in a basin, and moist silver oxide is added till it becomes neutral; the solution is quickly filtered; the residue washed for some time with boiling water; the filtrates, which generally soon begin to become turbid and brown from reduced silver, are immediately treated with hydrogen sulphide; and the acid liquid is concentrated on the water-bath. The crude gluconic acid thus

obtained is neutralised with milk of lime; the resulting calcium salt converted into a lead salt; and the pure acid obtained from the latter by decomposition with hydrogen sulphide.

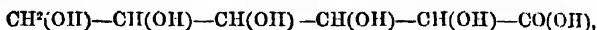
Gluconic acid is an acid syrup. Its calcium and barium salts and the ethylic ether crystallise well; the lead, cadmium and alkali-metal salts are amorphous.

Hlasiwetz and Habermann suppose that the formation of gluconic acid is preceded by that of a non-isolable chlorine-compound  $C^6H^{12}O^4.Cl^2$ , the two atoms of chlorine being subsequently replaced by one atom of oxygen.

Respecting the constitution and basicity of gluconic acid, different views have been advanced. Fittig (*Ueber die Constitution der sogenannten Kohlhydrate*, Tübingen, 1871) regards glucose as the aldehyde of a heptatonic alcohol  $C^6H^7(OH)^7$  derived from the saturated hydrocarbon  $C^6H^{14}$ , and therefore as having the constitution



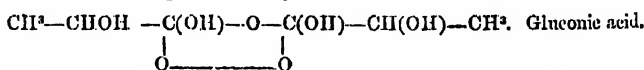
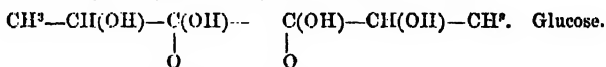
This, like all aldehydes, should yield by oxidation, an acid containing one atom of oxygen more, and differing from it in constitution only by having the last group  $CHO$  replaced by  $CO(OH)$ ; gluconic acid should therefore have the structure



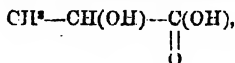
and should accordingly be monobasic.

Hlasiwetz, on the other hand (*Ann. Ch. Pharm.* clviii. 253), maintains that it is bibasic, and brings forward the following experiments in support of his view. When milk of lime is added to a moderately dilute lukewarm solution of monobasic calcium gluconate  $Ca(C^6H^{11}O^7)^2$ , as long as the lime dissolves quickly on agitation, the liquid then filtered, and the clear filtrate heated, the bibasic calcium salt  $CaC^6H^{10}O^7$  (dried at  $120^\circ$ ) separates immediately, and at the boiling heat almost completely, as a white indistinctly crystalline mud, which must be quickly filtered, washed and pressed. This salt dissolves easily in sal-ammoniac. The corresponding barium salt,  $BaC^6H^{10}O^7$  (at  $120^\circ$ ) is precipitated in white flocks on mixing the solution of monobasic calcium gluconate with baryta-water, and heating to the boiling point. The bibasic calcium and barium salts of lactic acid,  $C^3H^3O^3$ , are obtained by similar processes.

Regarding therefore gluconic acid as bibasic, Hlasiwetz suggests that glucose and gluconic acid may be represented by the following formulæ:



Glucose being, according to this view, a simple polymeride of  $\beta$ -lactic acid,



which, according to the experiments of Hoppe-Seyler, is formed from glucose by the action of caustic soda.

Fittig, however (*Ann. Ch. Pharm.* clix. 111), still maintains the monobasicity of gluconic and lactic acid. He points out that salicylic, paroxybenzoic acid, &c., exhibit exactly similar relations with lime and baryta, and that glycerin, mannite, glucose, cane-sugar, &c., form with lime and free bases in general, saline compounds, which are decomposed by carbonic acid, and that consequently the experiments of Hlasiwetz do not afford any satisfactory proof of the bibasicity of gluconic and lactic acid. Both these acids, when treated with carbonates, exchange only 1 at. hydrogen for metal and therefore contain only one hydroxyl group in combination with oxidised carbon; in other words, they are monobasic.

**GLUCOSE.** See SUGARS.

**GLUCOSIDES.** Schützenberger (*Compt. rend.* lxx. 350) has attempted to produce glucosides synthetically by means of the acetyl derivatives of the sugars. When sodium-saligenin and acetyl-glucose are heated together in presence of benzene or alcohol, there is produced a small quantity of a substance which forms glucose and saliretin on boiling with diluted sulphuric acid; this is obtained pure by evaporation to dryness, solution in water, precipitation by lead acetate, and decomposition by sulphuretted hydrogen and finally, by evaporation to dryness *in vacuo*, there is obtained



an amorphous yellowish brittle mass, soluble in water and alcohol. The greater part of the substances employed, however, react differently, aceto-saliretin  $C^{11}H^{11}(C^2H^3O)O^2(?)$ , and sodium glucate or glucinate being formed: the former, which yields saliretin and sodium acetate on saponification, is likewise obtainable by the action of acetic anhydride on saliretin.

*Diaceto-saccharose* and *sodium-saligenin*, heated in an open vessel, together with absolute alcohol, also form a small quantity of a glucoside which splits into glucose and saliretin; the greater portion of the substances, however, is converted into aceto-saliretin and the sodium salt of an acid  $C^{12}H^{12}O^6$ , very similar to glucinic or glucic acid (p. 556), which may be termed *saccharinic acid*. This sodium salt,  $C^{12}H^{12}NaO^6$ , separates in small white crystals from boiling absolute alcohol; it is very soluble in water, gives with basic lead acetate a precipitate soluble in excess of the acetate, and yielding the acid itself by decomposition with sulphuretted hydrogen; the acid forms a very sour syrup.

The lead precipitate obtained by treating saligenin with lead acetate also yields, when heated with an aqueous solution of acetyl-glucose or -saccharose, a considerable quantity of a glucoside which splits into saliretin and glucose on treatment with acids; it is, however, uncrystallisable.

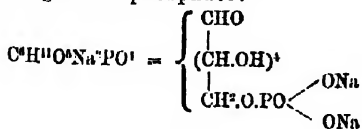
*Rhamnetin* (obtained by boiling rhamnegin, its glucoside, with dilute sulphuric acid) dissolved in caustic potash to saturation gives a precipitate with lead acetate; this precipitate heated in sealed tubes to  $140^\circ$  with solution of *diacetyl-saccharose*, gives a colourless liquid containing glucose, and a yellow insoluble portion which is a mixture of rhamnetin and the lead-compound of its glucoside; this portion treated with sulphuretted hydrogen, after thorough washing, yields a dark yellow liquid, from which an easily soluble amorphous dark yellow dye-stuff is obtainable by evaporation; this is extremely like rhamnegin in its properties, dyes the same tints, and splits on boiling with acids into glucose and rhamnetin, which is insoluble in water.

**GLUCOSO-PHOSPHORIC ACID,  $C^6H^{12}PO^4$**  (Amato, *Gazzetta chimica italiana*, i. 56).—This acid was prepared from a strongly acid residue which Schiff obtained in the course of his researches on the constitution of salicin and helicin, by treating the latter substance with phosphorus oxychloride, digesting the resulting mass with alcohol, and evaporating. This residue—which must have been produced by the mutual action of hydrochloric acid, phosphoric acid, and glucose, resulting from the decomposition of helicin in presence of phosphorus oxychloride—was rendered slightly alkaline with sodium carbonate, then evaporated to a syrup, and digested with alcohol, which partly dissolved it, leaving a residue of chloride and phosphate of sodium. On distilling off the alcohol, evaporating the residue at a very gentle heat, and treating it with absolute alcohol, there remained a quantity of sodium phosphate nearly free from chloride. On again distilling off the alcohol and evaporating, a residue was obtained which dissolved completely in absolute alcohol; and this substance, when freed from alcohol and evaporated under the air-pump, formed an extremely hygroscopic mass, which became pasty on exposure to moist air, but was very friable and easily pulverised when dry.

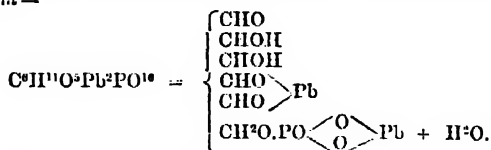
This substance is very soluble in water and alcohol, but insoluble in ether; it has a yellowish tinge when first obtained, but may be rendered perfectly white by boiling with animal charcoal. It does not precipitate barium chloride or lead acetate, and may be purified from a small quantity of phosphoric acid, adhering to it in the form of sodium phosphate, by treating it with lead acetate, evaporating, dissolving the residue in absolute alcohol, evaporating off the alcohol, and precipitating the excess of lead with hydrogen sulphide.

The aqueous solution does not give the reaction of phosphoric acid with magnesium salts, ammonia and sul-ammoniac; neither does it exhibit the reaction of glucose with a cupro-potassic solution. But if it be previously boiled with a sufficient quantity of sulphuric acid, taking care not to carry the action so far as to destroy the glucose, the solution will then exhibit very plainly the reactions of phosphoric acid and of glucose. The presence of phosphoric acid may also be demonstrated by incinerating the substance, oxidising the residue with nitric acid, and testing as above with a magnesium salt and ammonia.

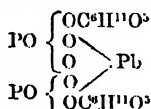
Quantitative determinations of the ash (sodium pyrophosphate) thus obtained, and of the phosphoric acid contained in it, show that the substance in question has the composition of disodic glucoso-phosphate:—



A lead salt was prepared by treating the sodium salt with excess of dilute sulphuric acid, digesting with alcohol to separate the acid sodium salt thereby produced, evaporating off the alcohol, neutralising with sodium carbonate, and finally with precipitated oxide of lead, and evaporating the filtered solution. A crystalline salt was thus obtained having an alkaline reaction, and yielding by incineration 75.4 p.c. ash, agreeing with the formula —



By treating sodium glucoso-phosphate with sulphuric acid, &c., in the same manner as above, excepting that the last traces of acidity were not neutralised with oxide of lead, a slightly acid crystalline lead salt was obtained, insoluble in ether, very soluble in water and in alcohol, and crystallising from the latter in magnificent setaceous needles, melting at 187°. This purified salt yielded 51.5 p.c. ash, agreeing with the formula  $\text{C}^2\text{H}^2\text{O}^3\text{Pb}^2\text{PO}^4$ . It may be supposed to be formed from 2 mol. of glucoso-phosphoric acid, which, under the influence of the lead salt, unite together, with elimination of 1 mol. water. Such a constitution is represented by the formula.—



In accordance with this, it is found that the ash gives the reactions of plumbic metaphosphate, whereas that of the former salt gives those of the pyrophosphate.

The last-described salt, heated to 150° in sealed tubes with ethyl iodide, was converted into lead phosphate and another substance, probably identical with that which Berthelot obtained by heating cane-sugar in sealed tubes with potash and ethyl bromide (*Jahresb. f. Chem.* 1860, 509).

**GLUTAMIC ACID**,  $\text{C}^2\text{H}^2\text{NO}^4$ , is produced, together with aspartic acid, by the action of boiling dilute sulphuric acid on vegetable proteids (p. 110). According to Masiwetz u. Habermann (*Chem. Centr.* 1872, 535) it is also produced from animal proteids by treating these bodies with hydrochloric acid, and decomposing the product with silver oxide. According to measurements by vom Rath, it crystallises in rhombic tetrahedrons having the axes  $a : b : c = 0.80115 : 1 : 1.1788$ . The right tetrahedron is usually present alone, sometimes, however, in combination with the left. Its specific rotatory power is  $+34.7^\circ$  (Ritthausen, *J. pr. Chem.* [2], v. 354).

**GLUTANIC ACID**,  $\text{C}^2\text{H}^2\text{O}^4$ , the homologue of malic acid, which Ritthausen obtained by the action of nitrous acid on glutamic acid (1st Suppl. 637), is a substance possessing very few characteristic properties. It forms an indistinctly crystalline mass, and its salts are amorphous. The specific rotatory power of the acid is, according to Ritthausen,  $-9.15^\circ$ .

**Deoxyglutanic acid**,  $\text{C}^2\text{H}^2\text{O}^4$ , is produced by heating glutanic acid with four times its weight of concentrated hydriodic acid to 120° for about eight hours. It is very readily soluble in water, alcohol, and ether, and crystallises exceedingly well, forming large, transparent monoclinic crystals, melting at about 97° and decomposing above 280° into water and the anhydride.

**Acid ammonium deoxyglutamate**,  $\text{C}^2\text{H}^2\text{O}^4 \left\{ \begin{array}{l} \text{H} \\ \text{NH} \end{array} \right\}$ , is obtained, by evaporating a strongly ammoniacal solution of the acid under an exsiccator, in transparent concentrically grouped crystals. **Calcium deoxyglutamate**,  $\text{C}^2\text{H}^2\text{CaO}^4 + \text{H}^2\text{O}$ , is sparingly soluble in water, and forms opaque laminae. **Barium deoxyglutamate**,  $\text{C}^2\text{H}^2\text{BaO}^4 + 5\text{H}^2\text{O}$ , crystallises in small transparent needles, readily soluble in water. **Lead deoxyglutamate**,  $\text{C}^2\text{H}^2\text{PbO}^4$ , is a white heavy precipitate, and the silver salt,  $\text{C}^2\text{H}^2\text{Ag}^2\text{O}^4$ , a very bulky precipitate resembling alumina; it is but sparingly soluble in boiling water, and separates in the crystalline state on cooling. It may be obtained in distinct needles by boiling a dilute solution of the acid with silver carbonate; but the greater part of the salt remains behind with the excess of silver carbonate.

Deoxyglutanic acid is isomeric with pyrotartaric acid, from which it follows that glutamic acid is not identical with either of the three homomalic acids derived from aconitic acid, as these latter would yield pyrotartaric acid by reduction.

**GLYCANILOSALHYDRANILIDE**,  $C^{23}H^{26}N^2O^3$ .—A compound obtained by boiling helicin with anilino (see HELICIN).

**GLYCERIC ACID**,  $C^3H^5O^3$ . When this acid is treated with phosphorus pentachloride, and the resulting chloride is gradually decomposed by water, as by exposure to a moist atmosphere, an acid is obtained, the lead salt of which has nearly the composition of a basic salt of chloropropionic acid. On the other hand, when poured into water, it yields a mixture of two acids, one of which contains chlorine.

When in the preparation of the chloride any notable rise of temperature is avoided, a product is obtained, which gives a clear solution when poured into water. But when gradually heated to  $150^\circ$ , the resulting compound gives with water a white thick syrup. This syrup gradually assumes the consistence of honey, and becomes transparent. The honey-like body, decomposed by baryta-water, yields barium monochlorolactate.

The product of the decomposition of the chloride by alcohol, submitted to fractional distillation, gives a colourless aromatic liquid, boiling between  $185^\circ$  and  $190^\circ$ , besides two other fractions having an oily consistence. The analysis of the principal product, although giving very discordant numbers, showed that it was probably ethyl dichloropropionate (Werigo a. Okulitsch, *Ann. Ch. Pharm.* cxlvii. 49).

*Ethyl Glycerate*,  $C^2H^3(C^2H^3)O^3 = C^2H^3O(OH)^2(OC^2H^3)$ , is obtained by heating concentrated glyceric acid with 3–4 vol. of absolute alcohol for some hours to  $170^\circ$ – $190^\circ$ . It is a thick, sticky, colourless liquid, which boils at  $230^\circ$ – $240^\circ$ , and has a bitter taste. On treating it with a mixture of nitric and sulphuric acids, the compound  $C^2H^3(OC^2H^3)(NO^2)^2$  is obtained, as a heavy colourless oil (L. Henry, *Deut. Chem. Ges. Ber.* iv. 701).

**GLYCERIN**,  $C^3H^5(OH)^3$ . This liquid boils without decomposition at  $179.5^\circ$  under a pressure of 12.5 mm., and at  $210^\circ$  under a pressure of 50 mm. It absorbs from the air varying quantities of water, up to  $50^\circ$  p. c. (Bolas, *Chem. Soc. J.* [2], ix. 84).

*Analysis of Commercial Glycerin*.—Commercial glycerin frequently contains glyceric ethers, volatile fatty acids, and other undetermined bodies. The action of nitro-sulphuric acid on these impurities is to convert them into bodies which are soluble in water, while the glycerin is transformed into nitroglycerin, which is insoluble. The nitroglycerin is washed, first with a dilute solution of caustic soda, afterwards with water, and subsequently dried in a water-bath. Before being dried it is mixed with its own bulk of wood-spirit, to assist in the volatilisation of the water present. From the weight of nitroglycerin found, may be calculated the amount of pure glycerin present in the sample. 100 grams of glycerin chemically pure, and concentrated at  $120^\circ$ – $150^\circ$  *in vacuo* were found to yield 190 grams of pure nitroglycerin: the theoretical yield is 247. Careful attention to the strength of acid used, the temperature, and all other details are necessary to ensure constant results (Champion a. Pellet, *Bull. Soc. Chim.* [2], xix. 494).

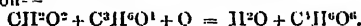
*Glycerin as a Solvent*.—According to Klover (*Chem. Centr.* 1872, 434) 100 parts by weight of glycerin dissolve at ordinary temperatures—

Parts by weight		Parts by weight	
20	.. Arsenious oxide.	6.70	.. Cinchonine sulphate.
20	.. Arsenic oxide.	10	.. Cupric acetate.
10	.. Benzoic acid.	30	.. Cupric sulphate.
10	.. Boric acid.	7.50	.. Mercuric chloride.
15	.. Oxalic acid.	20	.. Morphine hydrochloride.
50	.. Tannic acid.	0.20	.. Phosphorus.
40	.. Alums.	20	.. Lead acetate.
20	.. Ammonium carbonate.	50	.. Potassium arsenate.
20	.. Ammonium chloride.	3.50	.. Potassium chlorate.
5.50	.. Tartar-emetic.	25	.. Potassium bromide.
3	.. Atropine.	32	.. Potassium cyanide.
33	.. Atropine sulphate.	40	.. Potassium iodide.
10	.. Barium chloride.	0.50	.. Quinine.
2.20	.. Brucine.	0.25	.. Quinine tartrate.
5	.. Calcium sulphide.	50	.. Sodium arsenate.
0.50	.. Cinchonine.	8	.. Acid sodium carbonate.
27	.. Mercuric cyanide.	60	.. Borax.
1.9	.. Iodine.	98	.. Sodium carbonate.
0.45	.. Morphine.	20	.. Sodium chlorate.
20	.. Morphine acetate.	0.10	.. Sulphur.

Parts by weight		Parts by weight	
0.25	.. Strychnine.	1	.. Veratrine.
4	.. Strychnine nitrate.	50	.. Zinc chloride.
22.50	.. Strychnine sulphate.	40	.. Zinc iodide.
50	.. Urea.	35	.. Zinc sulphate

**Oxidation.**—In preparing glyceric acid by oxidising glycerin with nitric acid according to Beilstein's method (ii. 876), Heintz (*Ann. Ch. Pharm.* clii. 325) has obtained, as further products of the oxidation, racemic, formic, glycollic, and oxalic acids. The nitric acid of sp. gr. 1.5 and the glycerin having been left to mix gradually and then evaporated to a syrup over the water-bath, the crude glyceric acid thereby produced was gradually neutralised with lead oxide, and the precipitates obtained by partial precipitation were separately analysed. The first of these precipitates consisted of oxalate, the later ones of racemate. The glycollic acid is found, together with a considerable quantity of glycerin, in the mother-liquor from which the glycerate of lead has crystallised out. Heintz supposes that the glyceric acid,  $\text{C}_3\text{H}_5\text{O}_6$ ,  $\text{COOH}$ , which is the first product of the oxidation of glycerin by nitric acid, takes up 1 atom of oxygen, whereby its middle term is removed as formic acid, while the two exterior terms unite to form glycollic acid. The latter is then successively oxidised to glyoxylic and oxalic acids.

The formation of racemic acid,  $\text{C}^*\text{H}^*\text{O}^*$ , from glycerin, which contains only 3 at. carbon, might be attributed to the simultaneous oxidation of glyceric and formic acid, according to the equation—



The occurrence of formic acid among the products of the oxidation of glycerin by nitric acid was observed, indeed, by Huppert (*Jahresb. f. Chem.* 1863, 502), and has been confirmed by Heintz. The latter, however, did not succeed in producing racemic acid by the direct action of nitric acid on a mixture of glyceric and formic acids, or by oxidising glycollic acid with nitric acid, whereby racemic acid might possibly be formed, according to the equation,  $2\text{C}^*\text{H}^*\text{O}^3 + \text{O} = \text{H}^2\text{O} + \text{C}^*\text{H}^*\text{O}^6$ .

**Conversion of Glycerin into Acetone.**—The product obtained by the action of bromine on dichlorhydrin consists, according to Carius, of dichlorodibromacetone. By acting upon it with zinc and dilute sulphuric acid, and heating from time to time, not above  $40^\circ$ , a slow reaction is set up, resulting in the formation of acetone and a bromine-compound (probably isopropyl bromide) not separable by distillation (O. Lange, *Deut. Chem. Ges. Ber.* vi. 98).

**Metallic Derivatives of Glycerin.** *Sodium-glycerin*,  $\text{C}_3\text{H}_5\text{NaO}^3 = \text{C}_3\text{H}_5(\text{OH})(\text{ONa})$  (E. A. Letts, *Chem. Soc. J.* [2], x. 450). When a fragment of sodium is placed in glycerin, little or no action is observed; but on heating the mixture, a rapid extrication of hydrogen takes place, the sodium becomes red-hot, and the glycerin decomposed and charred, evolving fumes of acrolein. If however the sodium be diluted with mercury and then caused to act on glycerin, the action proceeds with more regularity, and finally sodium-glycerin is obtained as a gummy mass, which solidifies on cooling, and on addition of alcohol, crumbles down into a white crystalline powder. The same body may be obtained by heating glycerin with dry sodium-alcohol: in this case, alcohol is set free, and a solid white substance remains.

But the best method of preparing the compound, and one which yields it in any quantity, consists in dissolving sodium in alcohol and adding glycerin. At first no change is observed, but in a few minutes minute crystals consisting of radiating stars are formed, and in a short time a white crust is produced on the sides of the vessel. This crust is broken up, thrown on a filter, well washed with alcohol, and dried in a press between blotting paper. This must be done as quickly as possible, as the body is exceedingly deliquescent. The desiccation is afterwards completed over sulphuric acid, but not in a vacuum.

The product obtained by either of these processes is a compound of sodium-glycerin with alcohol  $\text{C}_3\text{H}_5\text{NaO}^3 \cdot \text{C}^2\text{H}^5\text{O}$ , which, when heated in a current of dry hydrogen, gives up its alcohol and leaves pure sodium-glycerin.

Sodium-glycerin is a white amorphous powder, attracting moisture with the greatest avidity from the air; by water it is constantly decomposed into glycerin and hydrate of sodium. On heating it to  $245^\circ$ , it shows signs of fusion, but appears to decompose at the same time. Bromine acts powerfully on it, giving small quantities of bromine-derivatives. It is remarkable that in this reaction a large quantity of water is produced. Pentachloride of phosphorus, after a few moments' contact, also reacts with great energy, producing so much heat as to char the compound.

The principal product of the decomposition of sodium-glycerin by heat appears to be acrolein.

**2. Glyceri-manganous acids.**—P. Schottländer (*Ann. Ch. Pharm.* cli. 230)

has obtained two compounds which he regards as the sodium and strontium salts of an etheric acid derived from manganese dioxide as acid, and glycerin as alcohol. To prepare the sodium-salt, a quantity (=4 parts of dry substance) of hydrated manganese dioxide, recently precipitated from manganous acetate by chlorine, is introduced into a boiling mixture of 70 parts glycerin, sp. gr. 1.26, and 77 parts soda-ley, sp. gr. 1.38, and the boiling is continued for some minutes. The manganese oxide is thereby completely converted into the compound above-mentioned, which separates, for the most part, in the form of a precipitate, appearing chocolate-coloured under the violet another-liquor, but scarlet when removed, while the rest remains dissolved. To free this precipitate—which is very susceptible of the action of air containing carbonic acid, and of water—from the dissolved products, it is introduced into a flask which can be closed, and washed therein, first with spirit of 90 (vol.) p.c., then with highly rectified spirit, finally with absolute ether, and dried at 100°. The product amounts to 4 parts by weight.

The compound thus obtained is a yellowish-red mass, easily crumbled to a powder which feels like tale. After drying at 100°–110°, it loses nothing at 120°, but about  $\frac{1}{2}$  p.c. of its weight at 160°, becoming at the same time somewhat darker in colour. At 170°–175° it decomposes with evolution of empyreumatic substances. When set on fire at one point, it glimmers throughout its whole mass. By exposure to the air, it is gradually converted into a black unctuous mass. This decomposition is accelerated by direct sunshine; light appears also to exert a decomposing action, even in the absence of moisture. The salt dissolves in cold water to a yellow-red liquid, which soon becomes turbid, from separation of manganese dioxide. The same change takes place instantly on boiling: the colourless filtrate contains soda and glycerin. From some approximate determinations of glycerin, giving about 26 p.c.  $C^3H^5$ , and from the quantities of manganese and sodium given by analysis, the formula of the compound is inferred to be  $(C^3H^5)^2Na^2MnO^6$ . It is insoluble in alcohol, ether, chloroform, and ethyl acetate, sparingly soluble in alcoholic, easily in aqueous glycerin (1:1 vol.) The latter solution remains undecomposed for some hours at 15°. It forms dark-coloured precipitates, immediately with silver, lead, or mercurous nitrate, after some time with cupric sulphate and mercuric chloride. Its reactions with dilute sulphuric acid, concentrated nitric or hydrochloric or phosphoric acid, aqueous oxalic acid, and aqueous sulphurous acid, are very much what might be expected from a mixture of glycerin with  $MnO^2$  or  $Mn^2O^3$ .

The strontium salt,  $(C^3H^5)^2SrMnO^6$ , is obtained by dissolving 12 parts of crystallised strontium hydrate in 150 parts glycerin of sp. gr. 1.26, with aid of heat, boiling the solution with 3 parts of levigated hydrated manganese dioxide, till the latter is transformed, and washing the product in a closed vessel, as described for the sodium-compound. It is a light ochre-yellow powder, appearing crystalline under the microscope, and behaving with reagents like the sodium-compound.

Attempts to prepare the potassium, barium and calcium salts of glyceri-manganous acid did not succeed, the manganese dioxide dissolving in the corresponding hydrates to liquids which did not yield any solid compounds.

**GLYCERYL CHLORONITROSULPHATE**,  $C^3H^5Cl(NO^2)(SO^2H)$ . This is a thick glutinous liquid, insoluble in water, obtained by treating glyceryl chlorosulphate with fuming nitric acid, or by acting on epichlorhydrin with a mixture of nitric and sulphuric acids (L. Houry, *Dent. Chem. Ges. Ber.* iv. 703).

**GLYCERYL OXIDE**, or **GLYCERYL ETHER**,  $C^3H^5O^2 = (C^3H^5)^2O^2$ . This body is formed, together with acrolein, propionic aldehyde, acetone, allyl alcohol, and a small quantity of phenol, by heating glycerin with calcium chloride. The phenol and glycerin-ether are contained in the portion of the product which boils between 180° and 190°, and may be separated by caustic potash, which dissolves the phenol.

The glyceryl ether, which remains undissolved, is a somewhat thick colourless liquid, smelling like spearmint, boiling between 169° and 173°, and almost completely soluble in 20 parts of water. Heated with water for four hours to 160°, it is converted into glycerin. On heating it gently with dilute hydrochloric or sulphuric acid, or a little zinc chloride, a strong odour of aldehyde is developed, and the distillate reduces an ammoniacal silver-solution. By heating it with a concentrated solution of potash, phenol is formed, besides volatile acids:  $C^3H^5O^2 + 2H^2O = C^3H^5O +$  (Linnemann a. von Zotta, *Ann. Ch. Pharm. Supplement-band*, viii. 254).

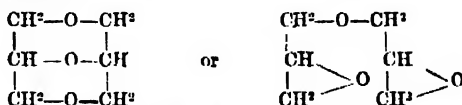
H. v. Gegerfeldt (*Dent. Chem. Ges. Ber.* iv. 919) by subjecting the residue left after the preparation of allyl alcohol from glycerin and oxalic acid, to distillation at a higher temperature, obtained a brown distillate, from which potash separated a liquid distilling between 160° and 280°, and yielding, after repeated rectification, a colourless somewhat viscid liquid, boiling between 170° and 172°, having a sp. gr. of 1.0007 at 18°, miscible in all proportions with alcohol and ether, and soluble in about its own volume of water. It agrees in composition and boiling-point with glyceryl ether, and

is regarded by v. Gegerfeldt as probably identical therewith: it appears, however, to be much more soluble in water than the product obtained by Linnemann a. von Zotta.

In some of its properties glyceryl ether resembles the monoallylin which Tollens obtained as a byo-product in the preparation of allyl alcohol from glycerin (p. 51); and indeed Linnemann a. von Zotta regard it as probably identical therewith. But monoallylin has the composition  $C^3H^5O^3 = (C^3H^5)^m \left\{ \begin{matrix} (OH)^3 \\ C^3H^5 \end{matrix} \right.$ , and boils at  $225^\circ-240^\circ$ .

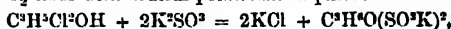
Moreover, when distilled with water it yields allyl alcohol, together with a viscid residue, whereas glyceryl ether yields nothing but glycerin; and finally bromine has no action on glycerin-ether, whereas it unites with allylin, forming a dibromide (Tollens).

v. Gegerfeldt suggests that glyceryl-ether may be represented by one of the following constitutional formulæ:



#### GLYCERYL-SULPHONIC ACIDS. 1. Glyceryl-disulphonic acid,

$C^3H^5O(SO^3H)^2 = C^3H^5 \left\{ \begin{matrix} OH \\ (SO^3H)^2 \end{matrix} \right.$ .—This acid is formed as a potassium salt by boiling dichlorhydrin for  $1\frac{1}{2}$  hour with neutral potassium sulphite:



(Schäuffelen, *Ann. Ch. Pharm.* cxlviii. 111); and, in like manner, from epichlorhydrin:



The potassium hydrate formed in this latter case exerts a further action on the epichlorhydrin (Pazschke, *Zeitschr. f. Chem.* v. 613). Thirdly, it is produced by heating sodium chloromethylisethionate with neutral sodium sulphite in a flask with reversed condenser:



The sulphuric acid and excess of sulphurous acid are removed by baryta-water, and the glyceryl-disulphonic acid is precipitated as barium salt by mixing the concentrated filtrate with barium chloride and leaving it to stand (Pazschke, *ibid.* vi. 512).

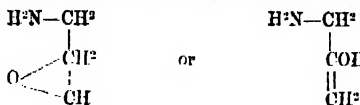
Glyceryl-disulphonic acid separated from its lead salt by hydrogen sulphide forms a syrupy liquid which does not crystallise, even after long standing over sulphuric acid. The potassium salt,  $C^3H^5O(SO^3K)^2 + 2H^2O$ , forms transparent colourless crystals, which (according to measurements by G. Werner) belong to the rhombic system, with the axial ratio  $0.41:0.48:1$ , and predominant octohedral faces, together with the perpendicular end-face and the rhombic prism. The salt dissolves sparingly in cold, easily in warm water. On mixing its boiling solution with barium chloride, *barium glycerin-disulphonate*,  $C^3H^5(OH)(SO^3)^2Ba$ , separates as a white anhydrous crystalline powder. This salt dissolves slowly in water, and the solution, when left to evaporate, deposits a bihydrated barium salt in white nodules which dissolve more easily in water. The calcium salt forms small hard crystals insoluble in alcohol. By treating the barium salt with ammonium carbonate, the ammonium salt is obtained in white, hard, very soluble crystals. The neutral lead salt, obtained by decomposing the barium salt with sulphuric acid, and saturating with lead carbonate, forms large transparent crystals,  $C^3H^5(OH)(SO^3)^2Pb + 2H^2O$ , very soluble in water. If, on the other hand, the acid be saturated with lead hydrate, an uncrystallisable *basic lead salt* is obtained, having an alkaline reaction and easily soluble in water.

The silver salt,  $C^3H^5(OH)(SO^3Ag)^2$ , forms white warty crystals slightly blackened by light, easily soluble in anhydrous, slightly in aqueous alcohol. The copper salt forms light blue crystals easily soluble in water (Schäuffelen).

*Glyceryl-trisulphonic acid*,  $C^3H^5(SO^3H)^3$ , is prepared by prolonged boiling of trichlorhydrin with potassium sulphite. On evaporating the resulting solution, the potassium salt crystallises out mixed with potassium chloride, from which it cannot be separated by crystallisation. The solution must therefore be mixed with sulphuric acid, and evaporated down; the residue exhausted with alcohol, and the solution of the free acid saturated with barium carbonate after boiling with water. On cooling, *barium glyceryl-trisulphonate*,  $[C^3H^5(SO^3)^3]^2Ba$ , separates as a white, crystalline powder, slightly soluble in water. By leaving the solution to evaporate, the same salt is obtained in more soluble crystals containing water of crystallisation.

**GLYCIDAMINE**,  $C^3H^7NO$  (Claus, *Ann. Ch. Pharm.* clxviii. 29).—A base produced, together with diamidohydrin (p. 319), by the action of alcoholic ammonium (containing 1 p.c.  $NH^3$ ) on dichlorohydrin. The *hydrochloride*,  $C^3H^7NO.HCl$ , which is the direct product of the reaction, may be obtained in crystals by precipitating the alcoholic solution with ether; it is very hygroscopic. The *platinochloride*,  $2(C^3H^7NO.HCl).PtCl_4$ , crystallises in transparent shining needles.

Glycidamine may be represented by the constitutional formula:—



It is probably identical with Berthelot a. De Luca's *glyceramine*, which they obtained by a similar process, and represented by the formula  $C^3H^7NO^2$ .

**GLYCOCHOLIC ACID.** For the preparation of this acid, Gorup-Besanez (*Ann. Ch. Pharm.* clvii. 286) recommends the following process as easier and more productive than those given by Strecker and by Hoppe-Seyler.

Ox-gall, fresh from the gall-bladder, is evaporated nearly to dryness in the water-bath, and the residue is exhausted with alcohol of 90 p.c. The alcohol is evaporated or distilled off; the residue, diluted, if necessary, with water, is treated with milk of lime and gently warmed, whereupon the greater part of the colouring matter is carried down with the lime; and the liquid is filtered and left to cool.

The filtrate, generally of a faint wine-yellow colour, is treated with dilute sulphuric acid, avoiding excess, till a permanent turbidity is produced. If it be then left at rest, the whole solidifies in a few hours to a mass of crystals of glycocholic acid, which is to be thrown on a filter (the filtration being best effected by the use of a water air-pump), washed with cold water, and pressed, first between blotting-paper, and then in a wooden screw-press. The acid thus obtained, which is generally colourless, may be further purified by dissolving it in a large quantity of lime-water, and adding dilute sulphuric acid till a permanent turbidity is produced. Perfectly pure glycocholic acid then separates out in needles of dazzling whiteness.

Hoppe-Seyler leaves the alcoholic solution of the acid to evaporate spontaneously, and purifies the residue by recrystallisation from alcohol. Gorup-Besanez, as well as Strecker, never obtained crystals in this way, but always a resinous mass. By his own method it sometimes happens that several hours after a permanent turbidity has been produced by sulphuric acid in the filtrate from the lime precipitate, a thickish oily mass is found at the bottom of the vessel, while the liquid above becomes gradually clear. After a few days or weeks, however, this mass becomes converted into crystals of glycocholic acid. The conditions which determine this anomaly have not been discovered.

**GLYCOGEN** (Kuhne, *Lehrbuch der Physiologischen Chemie*, Leipzig, 1866). Glycogen is best obtained pure by Brucke's method (*Wiener Acad. Berichte*, 1871), which readily separates all proteids from it. A solution of potassio-mercuric iodide is prepared by precipitating mercuric chloride with potassium iodide, washing the precipitate and then saturating a boiling solution of potassium iodide with it. A watery solution of glycogen, mixed with albuminous matters, is prepared in the ordinary way by cutting a perfectly fresh liver into pieces about the size of a hazel-nut, and throwing them into boiling water for a couple of minutes, so as to destroy the liver ferment, which would otherwise convert the glycogen into grape-sugar; the pieces are then bruised in a mortar and extracted with boiling water, and the solution is filtered. As soon as the filtrate is cold it is treated alternately with hydrochloric acid and the potassio-mercuric iodide solution as long as these agents produce any precipitate, and after standing for five minutes the solution is again filtered. Alcohol is then added until about 60 p.c. of absolute alcohol is present in the fluid: this throws down the glycogen alone, but more alcohol precipitates other bodies with it. The precipitate is collected on a filter, washed first with weak, then with 90 p.c. alcohol, and finally with ether, and is then transferred to a tile to dry. Glycogen is thus obtained as a snow-white amorphous powder; if impure or not quite dry, it forms a semi-transparent brittle mass.

The opalescent watery solution of glycogen passes unchanged through animal charcoal; it is four times more dextro-rotatory than solution of grape-sugar of the same strength. With solution of potassium iodide containing free iodine, it gives a deep red colour, which is removed by excess of glycogen; the colour also disappears on heating, but returns on cooling. Strong solution of caustic potash clears away the opalescence of the watery solution of glycogen, but produces no other change in it; the clear solution thus obtained dissolves cupric oxide, forming a deep blue solution

which is not reduced on boiling. Boiling with dilute nitric acid turns glycogen into oxalic acid, but similar treatment with sulphuric or hydrochloric acids converts it into grape-sugar; it is also turned into glucose by the action of saliva, pancreatic juice, blood-serum, and cold-water liver extract, all of which act most rapidly at a temperature of about 35°. The glucose is in each case preceded by a form of dextrin which has not yet been thoroughly examined.

Schetscherbakoff (*Deut. Chem. Ges. Ber.*, 1870) maintains that the glycogen which accumulates in the liver of an animal fed on mixed diet is not a single body, but a mixture of four substances, which can be separated by fractional precipitation with alcohol and ether, and differ in their rotatory power and their reactions with iodine and copper oxide. He calls them the *A*, *B*, *C*, and *D* forms. The last, treated with dilute sulphuric acid yields glucose; *C* gives *D* and glucose; *B* gives *C* and glucose, and *A* gives *B* and glucose. From these decompositions he concludes that the molecular formula of glycogen is at least  $C^{30}H^{50}O^{22}$ .

The question as to the origin and functions of glycogen in the organism is still far from settled; it seems to be present wherever active growth is going on, being found in most of the tissues of the young fetus, but, curiously, not in the liver. Dareste and Bernard (*Compt. rend.* 1871 and 1873) have both described its formation in the developing hen's egg, and state that it exists there in the form of granules much like those of vegetable starch. Glycogen would also appear to have some relation to the functional activity of the contractile organs; it exists in the muscles (McDonnell, Limpriht, Weiss, *Wien. Akad. Ber.* 1871) in considerable quantity, and partially disappears during muscular activity; alteration of diet and starvation affect its quantity in the muscles much later than in the liver; it also exists in the white blood-corpuscles as long as they exhibit their amoeboid movements, but is replaced by sugar as soon as the movements cease (Hoppe-Seyler, *Med. Chem. Unters.* 1871). There can be little doubt that the glycogen formed in the liver is constantly being converted into glucose during life, and carried off by the hepatic veins. The objections brought against this view are two: (1) the supposed absence of sugar in the perfectly fresh liver, and (2) the statement that as much sugar exists in the portal as in the hepatic blood. We know, however, that the kidneys, which certainly excrete urea, hardly contain a trace of that substance, a very small quantity only being present in them at any one moment, and we may expect to find the same true of the liver: that the latter organ, even in its freshest state, contains some sugar, has been shown by Dalton (*Trans. New York Acad. of Med.* 1871), who found that, though he could detect no sugar by Fehling's reagent in such quantities as from 100 to 150 grains of fresh dog's liver, yet that if he took 1,000 or 1,500 grains it could always be found. There is great contradiction among observers as to whether the blood of the hepatic veins contains more sugar than that of the portal vein; but probably one great cause of this error lies in the neglect of the precaution of ligaturing the portal vein close to the liver before taking the blood from it for analysis. If this is not done, on account of the free communication of the two systems, much blood from the hepatic veins is sure to flow back into the portal vein during the disturbance caused by the operation. When the portal vein is previously tied, most observers agree in stating that hepatic blood contains much more glucose than portal blood, the latter indeed containing none at all in animals fed on a purely albuminous food. Though the liver itself contains a ferment capable of transforming glycogen into glucose, this change would appear to be chiefly effected by the ferment in the blood: for it is much hastened by increased blood-flow through the organ, and it is probably chiefly thus that operations which cause paralysis of the vaso-motor nerves of the organ bring about artificial diabetes, more sugar passing then into the blood than can be used up by the organism. Experiment has shown that the introduction of grape-sugar into the blood of a rabbit in the proportion of 2 grams for each kilogram of the body-weight, will cause diabetes.

That the glycogen of the liver is formed, or at any rate can be formed, in that organ itself, from materials containing no sugar or starchy matters, has long been known; but the nature of the chemical changes which are concerned in its production is obscure. Whether or no it is normally formed from proteid food-stuffs, it certainly is formed from such when animals are fed on them alone, so that the idea suggests itself that these matters split up in the liver into a highly nitrogenised portion and glycogen. In support of this view, several observers have stated that the liver contains much urea, or, in the case of birds, uric acid (Meissner, Cyon), and have supposed these bodies to be in the main formed in that organ, and merely afterwards separated from the blood by the kidneys. This agrees with the fact that in many diseases of the liver, as acute atrophy, urea almost disappears from the urine. Cyon (*Centrbl. f. d. Med. Wiss.* 1870) passed defibrinated blood to and fro through the vessels of a fresh liver kept warm, and found the quantity of urea much increased by its passage; some doubt, however, attaches to his mode of determination of the quantity of urea, and Gscheidlen



(*Stud. über d. Ursprung d. Harnstoffs in Thierkörper*) found that, though the glycogen increases in quantity in a liver cut out and left to itself, the urea does not; he therefore concludes that the formation of the two substances goes on independently. Glycogen is also abundantly formed in the livers of animals fed on starch and saccharine food. As much fat then accumulates in the liver, it has been suggested that sugar may be decomposed in the organ, forming fats and glycogen.

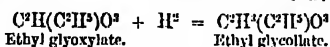
*Triacetyl-glycogen*, heated to 150° with excess of acetic anhydride, swells up without dissolving, and the product, after washing with water, consists of white amorphous triacetyl-glycogen,  $C^6H^4(C^2H^3O)^3O^3$ , insoluble in water, alcohol, ether, and acetic acid, and reconverted into glycogen by saponification (Schützenberger u. Naudin, *Deut. Chem. Ges. Ber.* ii. 163).

H. N. M.

**GLYCOL, DICHLORONAPHTHYDENCIC.** See NAPHTHALENE COMPOUNDS.

**GLYCOL, TOLYLENIC.** See TOLYLENE COMPOUNDS.

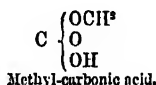
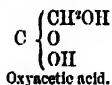
**GLYCOLLIC ACID,  $C^2H^3O^3$ .** This acid is formed, together with glyoxylic and tartaric acids, by the action of sodium-amalgam on an alcoholic solution of ethyl oxalate:—



The acid  $C^2H^3O^3$ , called *glycollic acid*, said by Friedländer to be produced in this reaction, appears to have no existence (Dobus, *Chem. Soc. J.* [2], x. 365).

Glycollic acid is also produced by the action of chlorine and water at ordinary temperatures on sorbin and levulose:  $C^6H^{12}O^8 + O^2 = 3C^2H^3O^3$  (Hlasiwicz u. Habermann, *Jahresb.* 1870, 840).

*Identity of Glycollic Acid from Different Sources.*—The experiments of Wurtz, Drechsel, Kolbe, and Kekulé (ii. 910), had indicated the probable existence of two modifications of the acid  $C^2H^3O^3$ , one crystallisable and non-deliquescent, the other liquid at ordinary temperatures, or at all events very deliquescent; and Kolbe suggested that these acids might be respectively—



To throw further light on this question, Fahlberg (*J. pr. Chem.* [2], vii. 329) has prepared glycollic acid from the mother-liquor of fulminating mercury, said by Cloez to be syrupy and uncrystallisable, and compared it with the acid obtained from other sources. The liquors were treated successively with sulphuretted hydrogen and milk of lime to remove mercury, oxalic acid, and glyoxylic acid, the latter being decomposed by boiling the liquid into glycollic and oxalic acids; carbonic acid gas was then passed through the liquid to precipitate the excess of lime, and the filtrate was evaporated to a syrup. Calcium glycolate then either separated in crystals or was thrown down by addition of alcohol, freed from acetate, formate, &c., by pressure, and purified by recrystallisation. By decomposing this salt with oxalic acid, mixing the filtered solution with lead carbonate, decomposing the resulting solution of lead glycolate with hydrogen sulphide, and evaporating the filtrate, glycollic acid is obtained in radiate groups of needles; and by dissolving these crystals in ether free from alcohol, and leaving the solution to evaporate in a vacuum, beautiful anhydrous laminae are obtained which melt at 80°, and are not at all deliquescent. If, however, too strong a heat is employed in the evaporation, or if the ether used as a solvent contains alcohol, no crystals are obtained, the crystallisation being prevented by the presence of glycollic anhydride (diglycollic acid) in the first case, and of ethyl glycolate in the second. In like manner the glycollic acid obtained from monochloroacetic acid (ii. 909) which, when separated from the silver salt, is very deliquescent, and when separated from the potassium salt appears quite uncrystallisable, may be obtained in fine permanent crystals by converting it into the calcium salt and separating it as above described. Hence it appears most probable that the syrupy or deliquescent acid obtained by several experimenters was more or less impure, and that there is actually but one glycollic acid.

Glycollic acid, from whatever source it may be prepared, is acted upon in the same manner by *phosphorus pentachloride*, yielding at ordinary temperatures glycollic

chloride,  $\text{CH}^2\text{OH}.\text{COCl}$ , and at  $120^\circ$ , chloroacetyl chloride,  $\text{CH}^2\text{Cl}.\text{COCl}$  (Fahlberg).

The action of hydrochloric acid on pure glycollic acid does not yield chloroacetic acid; the acid obtained by Kekulé's process from silver or potassium chloroacetate, however, yields chloroacetic acid in this way; but Fahlberg finds that this is simply *precontained* in the impure glycollic acid employed. Kekulé's production of bromoacetic acid by the action of hydrobromic acid on this impure glycollic acid is due to the reaction of the hydrobromic acid on the chloroacetic acid actually present. By heating glycollic acid with alcohol saturated with hydrochloric acid to  $150^\circ$ , glycollic ether is formed, but no chloroacetic acid.

**Metallic Glycollates.**—The calcium salt,  $\text{Ca}(\text{C}^2\text{H}^3\text{O}^2)^2$ , crystallises from concentrated solution in hard, translucent crystals, the form of which resembles that of the diglycollate. From dilute solutions it separates in concentrically grouped needles containing  $2\text{H}_2\text{O}$ , and soluble in 19 pts. water at  $15^\circ$ . The copper salt,  $\text{Cu}(\text{C}^2\text{H}^3\text{O}^2)^2$ , prepared by digesting the aqueous acid with cupric oxide and evaporating, forms splendid blue crystals sparingly soluble in cold, more soluble in hot water. The thallous salt,  $\text{TlO}(\text{C}^2\text{H}^3\text{O}^2)$ , prepared by treating the carbonate with aqueous glycollic acid, crystallises in anhydrous long-pointed needles. The zinc salt,  $\text{Zn}(\text{C}^2\text{H}^3\text{O}^2)^2 + 2\text{H}_2\text{O}$ , prepared in like manner, separates, after sufficient concentration, in warty groups of needles, soluble in 26 parts of cold water. The neutral and basic lead salts have the properties described in vol. ii. p. 911 (Fahlberg).

**Ethyl Glycollate.**  $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ , is prepared: 1. By heating equivalent quantities of calcium glycollate and potassium ethyl-sulphate to  $170^\circ$  (Fahlberg). 2. By gradually adding a solution of sodium ethylate to monochloroacetic acid, and heating the mixture for some time in a vessel with reversed condenser:



(L. Henry, *Dent. Chem. Ges. Ber.* iv. 706.) When purified by fractional distillation it is colourless, boils at  $150^\circ$  and has a sp. gr. of 1.033 (at what temperature?) (Fahlberg); 0.9770 at  $150^\circ$  (Henry). It is decomposed by water into alcohol and glycollic acid, and unites with calcium chloride, on which account anhydrous cupric sulphate must be employed for its dehydration (Fahlberg).

**Glycollic Anhydride, or Diglycollic Acid,**  $\text{C}^2\text{H}^3\text{O}^2 = \text{O}$ , is formed  
 $\text{CO}.\text{CH}^2\text{OH}$   
 $\text{CO}.\text{CH}^2\text{OH}$

by heating glycollic acid—in which case, however, the greater part of it suffers further decomposition, yielding the isomeric compounds, glycollide and dioxymethylene,  $\text{C}^2\text{H}^3\text{O}^2$  (ii. 912);—or better, by exposing the acid to the vapours of sulphuric anhydride. After a few days the anhydride is obtained as a lustreless powder which may be purified from glycollic acid by washing with water. It is insoluble in alcohol, ether, and cold water; boiling water reconverts it into glycollic acid and dissolves it. It melts at  $128^\circ$ – $130^\circ$ , that is to say, at a temperature midway between the melting points of glycollic acid ( $80^\circ$ ) and glycollide ( $180^\circ$ ). The presence of a small quantity of this compound prevents, as already observed, the crystallisation of glycollic acid (Fahlberg).

**GLYCOL-NITRINS.** See NITRINS.

**GLYCOL-METHYL-GUANIDINE.** See GUANIDINE.

**GLYCOSALHYDRANIDE,**  $\text{C}^6\text{H}^{11}\text{NO}^6$ . A compound obtained by gently heating helicin with aniline (see HELICIN).

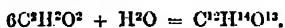
**GLYCYRRHIZIN.** To prepare this substance from its aqueous infusion, J. M. Hirsch (*Pharm. J. Trans.* [3], i. 749) adds acetic acid, evaporates to dryness, dissolves the residue in alcohol, and treats the solution with sodium carbonate, whereupon sodium acetate crystallises out, while glycyrrhizin remains in solution. Another method is to heat the alcoholic infusion of the root to boiling, filter, evaporate nearly to dryness, redissolve in alcohol, and again evaporate: the residue is nearly pure glycyrrhizin.

**GLYOXAL,**  $\text{C}^2\text{H}^2\text{O}^2$ . H. Schiff (*Gazzetta chimica italiana*, iv. 16) has prepared a condensation-product of this compound by the following process:—

When hydrochloric acid gas is passed for some time through a solution of glyoxal in five or six times its volume of strong acetic acid, and the liquid is then exposed in a closed vessel to a moderate heat, as by placing it near a lighted stove, a white crystalline substance separates in the course of the next day, on the sides of the vessel, and

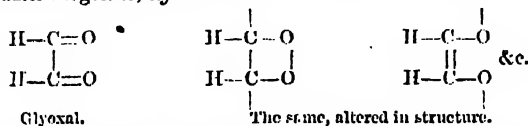
gradually fills the whole of the liquid. By pumping out the liquid, washing the residue with water, and drying it, a very white, microcrystalline powder is obtained, which, when agglomerated in lumps, is very much like potato-starch, crunches between the fingers, swells up in acetic acid, and, like starch, exhibits the greatest indifference to solvents and other reagents.

This substance is free from chlorine; after washing with water and drying, it gives by analysis 39.8 p.c. carbon and 3.6 hydrogen, agreeing with the formula,  $C^2H^4O^{12}$ , which is that of hydro-hexglyoxal, formed by the condensation of 6 molecules of glyoxal, with addition of 1 molecule water:

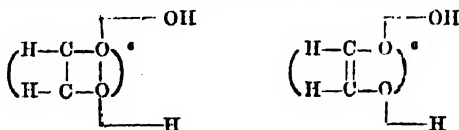


Hydro-hexglyoxal is insoluble in water, ether, benzene, petroleum, chloroform, and acetone; sparingly soluble in boiling alcohol. rather more soluble in concentrated acetic, sulphuric, and nitric acid; and is precipitated unaltered on addition of water. Heated with sulphuric acid, it gives off carbon monoxide, without a trace of acetic acid; neither does it yield acetic ether when heated with sulphuric acid and alcohol; it therefore does not contain any acetic residue. A further proof of this is afforded by the fact that it may be formed, though more slowly, by passing hydrochloric acid gas through a solution of glyoxalic ether. By prolonged boiling with water it acquires an acid reaction, and dissolves in the form of glycollic, and perhaps also of glyoxalic acid. The same transformation is produced much more rapidly by caustic alkalis, even in very dilute solution, and likewise by magnesia. No acetate is produced in either case.

Hydro-hexglyoxal, as already observed, is a very stable substance, and in particular does not exhibit any aldehydic reaction. Hence it cannot be supposed to contain the group,  $-CHO$ . To explain its stability, we must suppose that the aldehydic groups in glyoxal have undergone a change of structure, the oxygen- as well as the carbon-atoms having become united together, *e.g.* :-



Several of these groups may be supposed to unite together by virtue of their free affinities, the molecule of water at the same time serving to satisfy the two units of affinity which remain free, whatever may be the number of the aldehydic groups thus connected. In this manner compounds may be formed, represented by the formulæ:--



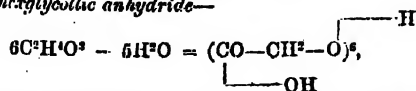
The first of these formulæ contains only one hydroxyl, whereas the second contains two. Now when hydro-hexglyoxal is boiled with excess of acetic anhydride, it partly dissolves, and the solution deposits, partly on cooling, further, on addition of water, a white powder, which gives off acetic ether when heated with sulphuric acid and alcohol, acetic acid when boiled with sulphuric acid alone; yields an alkaline acetate when boiled with dilute alkali; and gives by analysis (mean) 41.26 p.c. carbon and 3.98 hydrogen, agreeing very nearly with the formula,  $C^{12}H^{12}(C^2H^4O)^6$ ; it is, therefore mono-aceto-hydro-hexglyoxal. Prolonged boiling with acetic anhydride did not produce any derivative containing a larger proportion of carbon.

A corresponding *benzoyl derivative*,  $C^{12}H^{12}(C^7H^5O)^6$ , is formed by digesting hydro-hexglyoxal with benzoyl chloride.

These results show that hydro-hexglyoxal contains only one atom of hydrogen replaceable by acid radicals: it may therefore be regarded as a mono-acid alcohol.

Attempts to fix hydrogen upon it by the action of sodium-amalgam and of zinc and sulphuric acid were unsuccessful; concentrated hydriodic acid acts upon it, but the products of the reaction appear to be very complicated.

*Hexglycolide or hexglycollic anhydride*—



would be isomeric with hydro-hexglyoxal, but it has not yet been obtained.

**GÖTHITE.** Chrysoberyl, göthite, manganite and diaspore form an isomorphous group (rhombic) represented by the general formula  $M''(R^2)''O^4$ , in which, for chrysoberyl,  $M = G, Fe$ ;  $R = Al, Cr$ , while the others contain  $H^2$  instead of  $M''$ . Parallel with this rhombic group, and represented by the same formula, is the spinel group in the regular system (Kayser, *Jahresb. f. Chem.* 1870, 1281).

**GOLD.** Analyses of native gold from various localities in the British Isles are given by D. Forbes (*Phil. Mag.* [4], xxxiv. 331; xxxviii. 321):

A, from the Clogau quartz-vein No. 2, in Wales; B, wash-gold from the Mawddach river near Gwyn-fynydd. C, from St. Austell Moor, Cornwall. D, wash-gold from Wicklow in Ireland. E, *a* and *b*, from the Kildonan Valley, Sutherlandshire:—

	Au	Ag	Cu	Fe	SiO <sub>2</sub>	Total	Sp. gr.
A { <i>a</i>	90.16	9.26	trace	—	0.32	99.74	17.26
A { <i>b</i>	89.93	9.24	—	trace	0.74	99.81	15.62
B	84.80	13.99	—	0.34	0.43	99.65	15.79
C	90.12	9.05	—	—	0.83	100.00	16.52
D	91.01	8.85	—	—	0.14	100.00	14.34–15.07
E { <i>a</i>	81.11	18.45	—	—	0.44	100.00	15.799
E { <i>b</i>	81.27	18.47	—	—	0.36	100.00	

The analyses A agree with the formula  $Au^4Ag$ . The remarkably low specific gravity of the gold from Wicklow (D) is due to the porosity of the specimens examined.

All these native golds are found in granite and in the copper pyrites, galena, and silver fahl-ore contained in it. The ores of the Poltimore mines in Devonshire, which contain gold to the amount of 30 to 60 grams per ton, appear also to be products of the oxidation of metallic sulphides, especially iron sulphide.

Gold from Venezuela was found by Williams (*Chem. News*, xxi. 84) to contain

Au	Ag	Fe	Cu	
93.58	3.69	1.60	0.65	= 90.53.

Specimens of gold from Vancouver Island and West Africa have been described and analysed by F. Wibel (*Jahrbuch f. Mineralogie*, 1873, 244). The specimen from Vancouver Island is a crystal about 7 mm. long, weighing 26.7 grams and having the form of a rhombic dodecahedron ( $\infty O$ ) prismatically elongated in the direction of one of its axes, as in a specimen from the Ural described by G. Rose. Sp. gr. 18.5 at 22°. Its analysis gave—

Gold.	Silver.	Copper.	Iron.	
91.86	6.63	1.00	0.51	= 100.

No mercury, lead, or other metals were found in it.

The specimens from West Africa, analysed by K. Wibel, consisted—*a*. Of gold in grains; *b*. Of gold-dust; *c*. Of gold obtained by washing from a flesh-coloured clay in the neighbourhood of Elmina:—

	<i>a</i> .		<i>b</i> .			<i>c</i> .
Gold	89.40	87.91	97.23	96.40	92.03	97.81
Silver	10.07	11.40	2.77	3.60	5.82	2.19
Copper	0.53	0.69	—	—	2.15	—
	100.00	100.00	100.00	100.00	100.00	100.00
Sp. gr.	14.63	16.20				

Other specimens of West African gold, containing 4.15 and 25 p.c. of copper, and variable quantities of zinc, tin, and lead, were found to be adulterated with brass.

R. Brough Smith (*Sill. Am. J.* xlix. 263) gives a description of the Gold Fields of Victoria in Australia, in which he maintains, in opposition to Murchison, that the richness in gold of the quartz-veins, as well as their thickness, increases with their depth below the surface.

**Extraction.**—Rivot (*Ann. Min.* [6], viii. 1), describes the occurrence of gold and silver ores in California, and the mode of working them for the extraction of these metals. The gold occurs partly in quartz-veins, partly associated with quartz and pyrites. In the former, the whole of the gold is metallic; the latter ores do not yield up the whole of their gold to the amalgamation process—a proof that part of it is in a state of combination.

The silver ores, occurring in beds of slate, quartz, and heavy spar, rarely in calc spar, contain the silver in combination with sulphur, with arsenic and sulphur, or with antimony and sulphur, and are accompanied by varying quantities of blende, galena, iron pyrites, arsenical pyrites, bournonite, fahl ore, grey antimony ore, &c.

The processes employed at the present time in America for the extraction of gold and silver from mineral veins are: (1) Amalgamation in heaps; (2) amalgamation at 100° C. in copper pans; (3) direct amalgamation in pans by the aid of water, a process which is inexpensive, as it can be effected without material loss of mercury, but which does not yield so much gold and silver; and (4) amalgamation, preceded by the roasting of refractory ores with common salt. The yield of gold and silver from pyritic ores does not exceed 65 p. c. of the assay, which in itself is open to losses. According to many synthetical experiments, the loss is greater in assays of richer than of poor ores, amounting always to more than 30 p.c., and with fahlors and ores containing arsenical pyrites to more than 50 p.c. The loss incurred when working on a large scale is less than in laboratory assays. The difference between the yield on the large scale and the percentage indicated by the assay may exceed 30 p.c. even when the metallurgical method is quite perfect; but as the American methods are far from perfect, the difference is still greater.

A new process, devised by Rivot, has been worked in California with good results, and is said to be applicable to ores of every kind, giving at a small cost nearly the whole of the metal. It consists in roasting the ores with superheated steam before amalgamation. The action is somewhat sluggish in the case of pyrites and pyritiferous ores, but may be accelerated by addition of oxidising agents such as ferric oxides, roasted pyrites and black oxide of manganese.

The several stages of the process on the large scale are as follows:—

1. Roasting of the pyrites in heaps, or in reverberatory furnaces, in such a manner as to almost completely oxidise the metallic sulphides, and reduce the formation of sulphates to a minimum.
2. Pulverising and mixing of the roasted pyrites with the ores.
3. Roasting of the mixed mass with superheated steam in a revolving furnace, with exclusion of air.
4. Amalgamation in vortical mills, which are capable of a great out-turn, and of working wet or dry as may be desired, divide the mercury well, and effect a more speedy and complete amalgamation, owing to the pressure of the millstones.
5. Separation of the mercury from the residues.
6. Squeezing of the mercury through coarse linen bags, or wooden cylinders.
7. Distillation of the amalgam in cast-iron tubes provided with receivers cooled by water.

8. Smelting of the metals recovered by amalgamation in blacklead crucibles, and casting in iron moulds.

In the case of silver chloride and copper pyrites, the process has to be modified by the addition of iron pyrites. The several stages are then:

1. Mixing of the ores with iron pyrites, a small quantity sufficing for the chloriferous ores, whereas copper pyrites requires to be mixed with an equal weight of iron pyrites.
2. Roasting the mixture at a low red heat with superheated steam as long as sulphuretted hydrogen continues to escape.
3. Amalgamation of the roasted ores, with addition of water.
4. Separation of the amalgam, expression and distillation of the mercury, fusion of the noble metals, &c.
5. Working of the ore, after treatment with mercury, for copper in the usual way.

W. Skye (*Chem. News*, xxii. 282) has observed that grains of gold often resist the amalgamating action of mercury, in consequence of the gold becoming united on the surface with sulphur. Direct experiments showed that gold immersed in moist hydrogen sulphide or in a solution of ammonium sulphide, becomes converted on the surface into gold sulphide without any alteration in the colour of the metal. In the working of auriferous sand, the hydrogen sulphide which produces this change may be produced by the action of ferrous sulphate on various metallic sulphides. The gold thus altered may be rendered capable of amalgamation with mercury by ignition, especially if it does not contain any considerable quantity of copper (more than 7 p.c.). Gold may also be freed from its layer of sulphide by treatment with potassium cyanide, chromic acid, nitric acid, or an acid solution of calcium chloride.

A process devised by Tossé du Mothay for extracting gold and silver from arsenio-sulphides of lead, copper, &c., is described by G. Widemann (*Chemical News*, xxxiii. 126). The following are its main features:—

1. The sulphur ores are roasted with silicates, litharge being added to complete the oxidation.
2. The easily fusible scoria thus obtained is run on to a bath of molten lead, with which it is thoroughly mixed by mechanical means. The molten lead is said to dissolve out the whole of the gold and silver. The scoria is then removed, and fresh charges of the fusible silicates are added until the lead becomes sufficiently rich for cupellation.

3. The siliceous scoria is reduced by charcoal and iron, and an alloy of lead and antimony obtained.

4. This alloy is freed from antimony by acting on it at a high temperature with steam, which oxidizes the antimony. The lead is freed from all traces of antimony by means of a small quantity of lead sulphate.

Should the alloy contain copper instead of antimony, lead sulphide is added, and the resulting scoria of copper sulphide is removed. The pure lead thus obtained is either sold or used in the treatment of fresh ore.

*Reduction of Gold.*—Daintree first observed that when gold is introduced into a solution of auric chloride and the latter is reduced by organic substances, all the precipitated gold is deposited on the immersed metal. C. Wilkinson afterwards found that gold is precipitated under similar circumstances on the sulphides of copper, iron, arsenic, lead, zinc, molybdenum, and tungsten. According to Skoy (*Chem. News*, xxiii. 232) this latter result is due to the fact that all the sulphides above-mentioned, when immersed in a solution of gold, become covered with a thin film of gold and then act like an immersed bar of the metal. He finds also that this reduction may be effected by the sulphides of tin, mercury, bismuth, platinum, and gold. Instead of auric chloride, a solution of auric oxide in potash, sodium bicarbonate, or an alkaline silicate may be used. A solution of auric oxide in ammonia is not reduced below 200° F. A solution of gold sulphide remains unattacked under all circumstances.

*Spongy Gold.*—Gold may be precipitated in the spongy state by saturating a cold 10 p.c. solution of auric chloride with potassium bicarbonate, then adding 1 mol. bicarbonate and 5 mol. oxalic acid, and boiling (Prat, *Dingl. pol. J.* cxvi. 583).

*Detection and Estimation of Gold.*—In substances containing very small quantities of gold, the detection and estimation of the metal may be effected by means of tincture of iodine or bromine-water. The substance under examination is brought in contact with an equal volume of either of these reagents, and after some time filtering paper is soaked with the clear supernatant liquid. This paper when dried and burnt, leaves, if gold is present, a red ash. This process is particularly well adapted to the separation of gold from sulphides, inasmuch as these compounds are rendered so porous by the previous roasting that the solvent easily takes up the whole of the gold, while only very small quantities of either substance pass into solution (W. Skoy, *Chem. News*, xxii. 245).

*Detection of Gold in Sea-Water* (Sonstadt, *Chem. News*, xxvi. 150).—Experiments made on specimens of sea-water collected at various times at Ramsey Bay, Isle of Man, prove that gold exists therein, but as the quantity is certainly less than one grain in a ton, it is too small to admit of separation, or even detection, by the usual tests. Besides the difficulty of detection arising from the small quantity of gold present, there is another difficulty of a graver kind, due to a continuous redissolution of the gold after it has been separated in the metallic state. This redissolution is owing to the separation of iodine under the influence of reducing agents upon the iodate of calcium, which Sonstadt has previously shown to exist in sea-water. Even if the reducing agent is added in large excess, oxidation takes place so rapidly under the continuous reproducing power of calcium iodate, that, sooner or later, according to the excess of reducing agent added, the stage arrives at which the iodine is set free, and the suspended gold is redissolved.

Of three entirely different methods employed, the following is one which may be performed upon so small a quantity of sea-water as 150 to 200 c.c. Two or three decigrams of pure ferrous sulphate are dissolved in the water, which is acidulated with two or three drops of hydrochloric acid. The solution is heated in a clean and well-glazed porcelain dish, over a small flame, so managed that the flame may touch the under part of the dish without causing ebullition. Under these circumstances a lustrous film of ferric oxide forms in the dish, commencing from the portion directly heated by the flame. The heat is continued without boiling, until the sea-water is evaporated to about half, or so long as the film increases in extent and in lustre. The liquid is then poured off, the strongly adherent film is rinsed with a little water, and then about 50 c.c. of strong chlorine-water is allowed to stand in the dish for an hour or two, after which it is slowly evaporated down (over the film) to a few drops, a drop of dilute hydrochloric acid being added towards the end of the evaporation. The liquid, which should be nearly colourless, is then poured into a test-glass containing a few drops of solution of stannous chloride, when, after a few minutes, it takes a bluish or purplish tint, which may be exactly matched by a drop or two of a suitably diluted solution of gold added to a corresponding proportion of tin-salt in another glass. The formation of the film depends upon the iron being in a particular state of oxidation, and it is best, after adding the ferrous sulphate and hydrochloric acid to the sea-water, to leave it exposed to the air for a few hours before heat-

ing the liquid to obtain the film. The chlorine-solution of the sea-water films may be dried up in a porcelain crucible with precipitated lead, and gold beads obtained by cupellation, after fusing the lead into a button with borax; but for this experiment at least half a litre of sea-water should be taken, and even then the bead obtained is too small to be weighed. Similar experiments in the same vessels, and with the same reagents, upon simple water, and on water containing chloride of sodium and alkaline sulphates, never yielded the slightest coloration with stannous chloride.

**Separation of Gold from Copper.**—The solution of the two metals in aqua regia is evaporated to dryness, the residue dissolved in water, the solution mixed with oxalic acid, then after standing for 48 hours, heated to the boiling point and neutralised by caustic potash added at short intervals. The potassium oxalate thus formed unites with the copper oxalate, forming a soluble double salt, and the gold in it is left in the pure state. Gold precipitated by oxalic acid from an acid solution containing copper is always contaminated with cupric oxalate (E. Pargotti, *Zeitschr. anal. Chem.* ix. 127).

**Separation of Gold from Silver Chloride.**—The silver chloride formed in the purification of argentiferous gold by means of chlorine gas, contains an appreciable amount of gold, to such an extent indeed, that the silver bullion obtained by the reduction of the chloride often contain as much as 18 p.c. of gold. The processes generally adopted for the removal of this gold do not give satisfactory results, but the separation may be advantageously effected as follows. The fused chloride is covered with a layer of borax, one-eighth to one-quarter inch in thickness, and sodium carbonate is gradually added on the top of this layer, in quantity varying from 16 to 20 oz. per 230 oz. of silver chloride operated on. The chloride is not stirred, but the metallic gold is allowed to subside to the bottom of the receptacle. 20 oz. of soda will generally produce a gold button weighing about 35 oz., assaying from 870 to 880, while the silver bullion subsequently obtained will contain 2 to 5 parts of gold in 10,000 parts. A second treatment with a much smaller quantity of soda renders the silver perfectly free from gold (Loebius, *Chem. News*, xxvii. 128).

**Gold Monochloride, or Aurous Chloride, AuCl.** The directions usually given for the preparation of this compound, and the descriptions of its properties are somewhat discordant. According to Leuchs (*J. pr. Chem.* [2], vi. 156) these discrepancies arise from decomposition taking place during the preparation. He finds that when trichloride of gold is heated, the evolution of chlorine does not cease as soon as the whole of the trichloride is converted into monochloride, as commonly stated, but may go on till the gold is completely reduced to the metallic state. This result he attributes to the action of moisture in the air, which, being absorbed by the hygroscopic trichloride, decomposes some of the monochloride already formed into metallic gold and trichloride, the moisture again acting upon fresh portions of monochloride, and so on. To prevent this decomposition he adopts the following process. Trichloride of gold is heated to 200°–300° on a sand-bath, care being taken to crush all lumps, and to bring fresh portions of the material constantly in contact with the basin by trituration with a pestle. The evolution of chlorine is very rapid: the liquefied red chloride becomes first brownish-red, then dirty brown, yellowish-brown and dry, afterwards greenish, and ultimately pure yellow. When the mass acquires a greenish colour, the temperature is lowered gradually to 180°. The evolution of chlorine still continues, and the end of the operation can be judged of only by the changes of colour. As soon as the powder appears of a pure full yellow, it is removed from the sand-bath, triturated till it ceases to smell of chlorine, and at once transferred to closed glass vessels. The product, after cooling, is pure yellowish-white.

A chloride, intermediate in composition between the mono- and tri-chloride, is formed by heating spongy gold with a solution of auric chloride, or by heating aurous and auric chlorides together (Prat, 1st Suppl. 653).

**Iodides.** Aurous iodide, prepared with aqueous hydriodic acid, dissolves in hydriodic acid saturated with iodine, and the solution, when evaporated at a gentle heat, deposits small rhombohedral crystals of auric iodide,  $AuI_3$  (Prat, *Compt. rend.* lxx. 840).

**Oxides.** When gold is treated with a quantity of aqua regia not sufficient to dissolve it, but containing excess of hydrochloric acid, and the solution is saturated with such a quantity of potassium bicarbonate that the precipitate redissolves, an orange-yellow solution is obtained which begins to show turbidity at 55°, deposits at 60° a light olive-green hydrate, and at 65°–95° a dark olive-green hydrate, the former containing 8 p.c. the latter 7.74 p.c. oxygen, answering to the composition  $Au_2O_3$ . This intermediate oxide of gold gives up its water of hydration on exposure to the air, and is converted into a nearly black, hard, heavy mass, having a conchoidal shining

fracture. It is not altered by light, gives off its oxygen at about  $250^{\circ}$ , dissolves very easily in hydriacids, and forms a dark-green solution with cold hydrochloric acid. It also unites, especially when heated with oxygen-acids; hydrofluoric acid combines with it, but does not dissolve it. When a solution of gold in excess of aqua regia in which the nitric acid predominates is supersaturated with potassium bicarbonate and heated, an oxide is obtained, orange-coloured when freshly precipitated, ochre-coloured after washing and drying, and containing 15 p.c. oxygen, which answers to the formula  $\text{AuO}^2$ . It is not altered by light, but gives up its oxygen, with sparkling, when heated to about  $200^{\circ}$  (Prat, *loc. cit.*).

**Oxy-salts.** *Aurous Sulphate* (?). When spongy gold is heated with a mixture of sulphuric and iodic acids ( $3\text{HI} \cdot \text{SO}^4 : 2\text{HIO}^3$ ) till the mixture has acquired a dark orange-colour, which takes place at  $300^{\circ}$ , the whole of the gold is oxidised, and the product, when dissolved in fuming nitric acid, gives, on dilution with water and heating, a copious brown precipitate, consisting of a gold sulphate, which is quickly altered by light, is very difficult to crystallise, has a dark purple-red colour when dry, and appears remarkably stable when heated. It is very hygroscopic, and is decomposed by a large quantity of water into insoluble aurous sulphate and auric sulphate, which remains dissolved (Prat). This last decomposition would seem to show that the salt is an auroso-auric sulphate.

*Auric Sulphate and Nitrate.*—It is stated by Gmelin and other authorities that a solution of auric oxide in nitric or sulphuric acid is rapidly and completely decomposed on dilution with water. From the experiments of A. H. Allen, however (*Chem. News*, xxv. 85), it would appear that the oxacid salts of gold are more definite and more stable in solution than they are usually supposed to be.

A solution of auric oxide in nitric acid gave, on dilution with water, a perfectly clear solution which answered to all the tests for gold. It decomposed very gradually by keeping, the oxide being deposited.

In like manner an aqueous solution of auric sulphate deposited but very slowly a portion of the metal, the decomposition in many instances being very slight, and never wholly complete, even after a long interval.

Finely divided gold, when heated with solid potassium permanganate and concentrated sulphuric acid, is rapidly dissolved, yielding a solution which is not precipitated at all on dilution, but gives, when tested with oxalic acid or ferrous sulphate, abundant evidence of the presence of gold. There would appear, then, to be no doubt that the gold exists in this solution in the state of sulphate.

When nitric acid is substituted for sulphuric acid, the gold is completely precipitated on the addition of water. Reynolds and Spiller are of opinion that in this latter reaction auric nitrate is not produced. Allen objects to this conclusion, and points out that the true cause of the reduction is the presence in the solution of nitrous acid, since, if a small quantity of permanganate be added before dilution, or if the acid liquor be boiled with a crystal of ammonium sulphate, precipitation of the gold does not take place.

This explanation is further strengthened by the fact that it is possible, by adding a few drops of fuming acid to a pure solution of auric nitrate, to cause an instantaneous precipitation of the metal.

**Gold and Silver Sulphide**,  $2\text{Au}^2\text{S}^3 \cdot 5\text{Ag}^2\text{S}$ . This sulphide is formed by the action of melted sulphur on a mixture of gold and silver in the fused state. It is a dark grey crystalline substance of sp. gr. 8.159, decomposed by heating in a stream of hydrogen. Fused with sodium carbonate it gives sodium sulphide, and apparently an alloy of gold and silver (Muir, *Chem. News*, xxv. 654).

**Gold Purple, or Purple of Cassius.** Macquer having observed that the purple of Cassius was deeper in colour the more gold it contained, considered it to be a mixture of stannic hydrate and metallic gold. But Proust, finding that when moist it dissolved in ammonia, and that it did not yield gold when treated with mercury, looked upon it as a true combination, consisting of aurostannous stannate mixed with varying proportions of stannic hydrate. Debray (*Compt. rend.* lxxv. 1026) considers both views to be wrong, and regards the purple as a 'lake' of stannic acid coloured by metallic gold, the gold being prevented by its union with the acid from being dissolved out by mercury, just as ordinary lakes will not yield up their colours to water.

Instead of preparing the purple in the usual way, it may be obtained by first precipitating stannic oxide by boiling together stannic chloride and sodium acetate, then adding gold chloride and potassium oxalate, and again boiling, when metallic gold will be precipitated upon the oxide. A similar colour is produced if alumina be substituted for stannic oxide. This seems to show that the purple is simply an oxide coloured by gold. That the purple should be soluble in ammonia is not surprising if it be admitted



to be chiefly made up of stannic oxide, which is soluble in ammonia in the cold. Elevation of temperature and desiccation diminish the solubility both of stannic oxide and of the purple. Moreover, the solution, which always appears turbid by reflected light, slowly deposits metallic gold. The latter could not, therefore, have been present as an oxide, since ammonia, in acting upon oxides of the precious metals, gives rise to products more or less complex, but the metal is never set free.

In the assay of silver containing a little gold and tin, there is often observed, on dissolving the metal in nitric acid, a substance very similar in appearance to the purple of Cassius. It is not, however, soluble in ammonia, and Debray thought that this might be due to the metal having been dissolved in hot acid, just as stannic oxide obtained by oxidising tin with hot acid, is also insoluble in ammonia. He therefore attacked, with nitric acid, at a very gentle heat, an alloy of silver, gold, and tin, and obtained a purple residue quite soluble in ammonia, showing the identity of this residue with the ordinary purple.

Debray appears to consider a 'lake' as standing midway between a mixture and a chemical combination.

#### GOLDEN SEAL. See HYDRASTIS.

**GRAIN, ANALYSIS OF.** The methods hitherto employed for the determination of starch and cellulose in grain give very discordant results. When the starch is dissolved by a solution of malt (Oudemans' method), much nitrogenous matter remains with the cellulose, and is not perfectly removed by treatment with potash, which, moreover, dissolves cellulose to an appreciable extent. Purified cotton-wool lost 4.54 p.c. when boiled with a 1.25 p.c. solution of potash, and afterwards with dilute acetic acid; and on repetition of the treatment, suffered a further loss of 2.6 p.c. When vegetable matter is acted upon in the cold by potassium chlorate and nitric acid (F. Schulze's method), the cellulose obtained is very pure; but purified cotton-wool loses 3.6 p.c. when treated in this manner. To avoid those sources of error, W. Pillitz (*Zeitschr. anal. Chem.* xi. 46) determines the vegetable fibre in grain by heating the flour with very dilute sulphuric acid in sealed tubes at 140°-145°; under such treatment cotton-wool loses only 0.4 p.c. His plan of analysis is as follows:—

8-10 grams of the flour are exhausted as quickly as possible with 1 litre of cold water, by means of a Reul's press, in which the flour lies on a filter-bed, and water is forced through it by means of a column 7 feet high. In the watery solution the total solid matter, ash, nitrogen, and sugar are determined. The undissolved flour is quickly dried, first in a vacuum, then, after being finely powdered, at 100°. 1 to 1.2 gram of the dried mass is then treated with 40 c.c. of very dilute sulphuric acid (3 to 3.5 c.c. of acid sp. gr. 1.16 diluted to 1 litre), and heated in a sealed tube for eight hours at 140°-145°. The cellulose is then collected on a weighed filter, washed with water, alcohol, and ether, dried, weighed, and its ash deducted; it contains only traces of nitrogen. In the solution sugar is determined by Fehling's method, and the amount found is calculated as starch. The heating in the sealed tube is repeated with 1 to 1.2 gram of the original meal. The sugar thus obtained represents starch plus sugar and dextrin; and by subtracting the starch and sugar previously determined, the amount of dextrin is found. Fat, total nitrogen, and ash are determined in the usual manner.

The following are analyses made by this method. The millet, buckwheat, and spelt, were free from their external shells; the other grains were in their ordinary marketable condition:—

100 parts dried at 100° contain —	Prince Albert Wheat	Browick's Wheat	Spelt	Rye	Millet	Barley	Oats	Maize	Rice	Buckwheat
Cellulose . . . .	3.07	4.76	3.38	4.22	4.28	8.88	18.08	4.82	.87	2.05
Starch . . . .	73.51	70.17	71.60	68.60	69.20	62.65	53.62	72.27	85.41	77.64
Dextrin . . . .	2.28	5.27	2.46	5.78	1.29	1.06	1.46	.83	1.27	—
Sugar . . . .	1.56	1.07	1.23	2.17	.52	2.71	.37	1.59	trace	—
Extractive matter undetermined	4.54	.81	3.00	3.50	.52	1.73	1.66	1.65	.12	3.65
Fat . . . .	2.03	1.79	2.72	2.52	4.79	3.08	4.92	5.03	.90	2.80
Albuminoids insoluble	10.89	12.93	10.77	10.60	16.23	14.28	12.13	9.05	10.01	7.40
Albuminoids soluble	.38	.96	2.63	3.87	1.86	2.05	2.69	2.16	.46	4.67
Ash insoluble . .	.69	.61	.60	.24	.64	1.23	2.73	.38	.45	.61
Ash soluble . . .	1.05	1.63	1.61	1.50	1.18	1.45	1.44	1.32	.51	1.09

2nd Sup.

**GRANITE.** From an examination of English and Irish granites, S. Haughton (*Proc. Roy. Soc.* xvii. 209) concludes that they are either eruptive rocks belonging to the formations from the Silurian to the carbonaceous, or metamorphic rocks. The eruptive granites contain orthoclase and albite, but no lime felspar; the metamorphic granites, on the other hand, contain orthoclase and a lime felspar, viz., oligoclase, but no albite.

The granites of central and western Scotland are metamorphic, like those of Donegal and Norway, with which, in fact, they are geologically identical; eruptive granite is met with only occasionally, as near Peterhead. The felspars are the same as in the English and Irish granites (Haughton, *Jahrbuch f. Mineralogie*, 1871, 83).

J. Lemberg (*Zeitschr. geol. Gesellsch.* xxii. 85) has analysed several series of the decomposition-products of Finland felspars and granites. The results show that, in the process of weathering, the bases RO, and especially CaO, diminish in proportion to  $Al_2O_3$ , whereas  $H_2O$ ,  $Fe_2O_3$ , and  $MgO$ , are taken up; or that, under the influence of water containing potash and magnesia, CaO and  $K_2O$  are exchanged for  $MgO$ ;  $Na_2O$  and CaO for  $K_2O$ . For the analyses, see *Jahresb. f. Chem.* 1870, 1353.

**GRANULITE.** Scheerer (*Jahrbuch f. Mineralogie*, 1873, 673-691). The true granulites form a class of rocks, sharply characterised by their petrographic constitution, which may be regarded as co-ordinate with that of the gneisses, consisting mainly of a fine-grained mixture of felspar and quartz, and distinguished by admixture of garnet (sometimes also of cyanite): they exhibit for the most part, notwithstanding their characteristic deficiency in mica, the parallel structure, and therefore the character, of a stratified rock. They may in fact be regarded as gneisses containing little or no mica, and having that mineral replaced by garnet.

In chemical constitution also, the granulites are sufficiently near to the gneisses to admit of their division into groups corresponding with the red, middle, and grey gneisses (or upper middle and lower plutonites). Scheerer has shown (*Zeitschr. d. Deutschen geologischen Gesellschaft*, xiv. 23-150), that the chemical constitution of these gneisses may be represented by the following formulae, and by the oxygen-ratios, degrees of silicatisation (ratio of number of molecules of silica to number of molecules of base) and percentage of silica, thence deduced:—

	Upper plutonite Red Gneiss	Middle plutonite Middle Gneiss	Lower plutonite Grey Gneiss
Chemical formula	$4RO.9SiO_2$	$4RO.9SiO_2 + 2(2RO.3SiO_2)$	$2RO.3SiO_2$
Oxygen ratio RO : $SiO_2$ }	1 : 4.5	1 : 3.75	1 : 3
Degree of sili- entisation }	2.25	1.875	1.5
Percentage of silica Mean	76-74 75	71-69 70	66-64 65

The following are analyses of seven Saxon granulites:—1. Reddish granulite from Penig, containing, in a fine-grained eutectic ground-mass, numerous small crystals and granules of red garnet: no perceptible trace of mica. 2. Greyish flesh-red granulite from Neudörfchen, similar in structure to the preceding, but containing also small granules of quartz and crystalline felspar. 3. Greyish-white granulite from Limbach; ground-mass fine-grained to compact, with splintery fracture, and containing, besides pale-red garnet, granules of an unknown black mineral, to which the greyish colour is due. 4. Grey granulite from Penig, similar to 3, but containing more of the black mineral. 5. Dark grey granulite from Burgstadt, containing brown granules of garnet and black scales of mica. 6. Light-grey granulite from Neudörfchen, rather fine-grained, containing granules of quartz and crystalline felspar, together with scattered crystals of garnet, and here and there scales of pinchbeck-brown mica, with traces of the black-mineral. 7. Greyish-white slaty granulite from Steinä near Harttha, shows distinct parallel structure. The ground-mass appears under the magnifying glass to be made up of parallel layers of quartz and felspar with brown garnet and scales of pinchbeck-brown and black mica imbedded. According to Förster's observations, this rock is the most abundant of all the true granulites, and, together with gneiss-granulite and trap-granulite, makes up by far the greater part of the granulite field of Saxony:—

*Analyses of Saxon Granulites.*

	SiO <sup>2</sup>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	
1. . . .	76.33	12.89	2.35	0.45	0.35	7.59	—	0.22	= 100.18
2. . . .	75.80	12.09	2.42	1.45	0.38	4.27	2.72	0.39	= 99.52
3. . . .	75.46	12.09	3.75	1.22	0.66	3.96	2.46	0.25	= 99.85
4. . . .	72.97	12.69	4.55	2.33	0.63	3.46	3.16	0.13	= 99.92
5. . . .	71.25	14.28	4.32	2.84	0.92	3.02	2.76	0.16	= 99.55
6. . . .	73.47	14.86	3.64	1.62	0.67	3.95	1.80	0.21	= 100.22
7. . . .	73.37	14.09	3.31	1.54	0.76	4.25	2.49	0.27	= 100.08

From these analyses may be deduced the following oxygen-ratios, RO : SiO<sub>2</sub>, and degrees of silicatisation:—

	Oxygen ratio			Degree of silicatisation		
	Found	Normal	Difference	Found	Normal	Difference
1. . .	1 : 4.74	1 : 4.50	+ 0.24	1.58	1.50	+ 0.08
2. . .	1 : 4.64	"	+ 0.14	1.55	"	+ 0.05
3. . .	1 : 4.47	"	— 0.03	1.49	"	— 0.01
4. . .	1 : 3.93	1 : 3.75	+ 0.18	1.31	1.25	+ 0.06
5. . .	1 : 3.56	"	— 0.19	1.19	"	— 0.06
6. . .	1 : 3.83	"	+ 0.08	1.28	"	+ 0.03
7. . .	1 : 3.90	"	+ 0.15	1.30	"	+ 0.05

These numbers show that the normal granulites are co-ordinate, partly with the upper plutonite (red gneiss), partly with the middle plutonite (middle gneiss), but they do not indicate the existence of any granulite representatives of the lower plutonite (grey gneiss). Granulites of the last-mentioned variety (with 64–66 p.c. silica) appear indeed to occur much more rarely and in less extent than the two more highly silicated classes, but not to be altogether wanting. At Ehrenberg in the Zschopenthal, for example, there occurs a grey-black granulite containing 65.4 p.c. silica; and a very dark grey-black granulite from Waldheim has been found to contain 65.5 p.c. silica. The latter contains, together with a large quantity of garnet, a small quantity of pinchbeck-brown mica; the former, on the other hand, contains garnet without mica, and its dark colour appears to be due to the black mineral. Parallel structure is visible in the latter, but not in the former.

On comparing the analyses of the granulites with those of the gneisses which they most nearly resemble, it is seen that they differ considerably from the latter in their amount of water. In the granulites 1–3, the average amount of water is 0.29 p.c., and in the granulites 4–7, it is only 0.19 p.c., whereas the average proportions of water in the normal upper and middle plutonites are respectively 1 and 1.5 p.c. This deficiency of water in the granulites is a simple consequence of the almost total absence of mica. The several species of mica are indeed the only hydrated constituents of plutonic silicious rocks, the proportion of water contained in them being between 4 and 5 p.c. Where they are absent, in rocks which have not undergone alteration, water is either absent or present in small quantity only; in the latter case its presence may be due to small scattered particles of mica imperceptible to observation, or to an incipient weathering of the felspar.

These facts lead to the conclusion that granulites have been formed from gneisses (plutonites) by a process of transformation which has removed the chemically-combined water of the latter. That this process has consisted in a more or less complete remelting, or at least in a softening of the mass by heat, may be inferred from the occurrence of crystalline garnet, which has been formed by dehydration of mica. Garnets, indeed, having the composition expressed by the general formula  $3(2\text{RO} \cdot \text{SiO}_2) + 2\text{R}'\text{O} \cdot 3\text{SiO}_2$ , may have derived their constituents from the micas, their formation being accompanied by that of felspar and cyanite, or one of the two, according to the composition of the mica. Certain dark magnesia micas having the composition  $3(2\text{RO} \cdot \text{SiO}_2) + 2\text{R}'\text{O} \cdot 3\text{SiO}_2$ , differ indeed from garnet only by the water included in the first member; and in the case of other magnesia micas,  $2(2\text{RO} \cdot \text{SiO}_2) + 2(\text{R}'\text{O} \cdot 3\text{SiO}_2)$ , the formation of garnet is nearly as simple. Less simple is the derivation of garnet from the more silicious potash micas; but even in this case it is possible, taking into account the

simultaneous formation of the minerals above mentioned, or perhaps of the black mineral before alluded to as occurring especially in the granulites 3 and 6, most probably as a product of the decomposition of mica.

In the granulite district of Saxony there occur, together with the true granulites above considered, chiefly the following rocks:—*a.* Gneiss-granulites (and granulitic gneisses), i.e., rocks more or less fine-grained and micaceous, but likewise containing garnet, forming, indeed, transition-stages between gneiss and granulite. *b.* Gneissos (and gneiss-granites). *c.* Granitos (together with granulitic granite, granitic granulite, and Förster's granular normal granulite. *d.* Trap-rocks, the so-called trap-granulites (together with gabbro).

From the oxygen-ratios and degrees of silicatisation of these rocks it is inferred (*a*) that the gneiss granulites, like the true granulites, are co-ordinate with the upper and middle plutonites; the gneiss-granulites of Waldheim, however, which contains 66.3 p.c. silica, is a representative of the lower plutonite or grey gneiss; (*b*) that the gneisses, which occur but sparingly, belong to the middle and lower plutonite; (*c*) that the granites, which occupy a large portion of the district, belong to the upper and middle plutonite; (*d*) that the trap-granulites, including gabbro and hypersthénite, which, as already observed, form, together with slaty normal granulite and gneiss-granulite, by far the greater part of the whole granulite field, exhibit oxygen-ratios  $2\text{RO} : 3\text{SiO}_2$  included between 1 : 1.49 and 1 : 1.36, that is to say, they are similar in constitution to the corresponding rocks in other localities.

From all the facts above detailed Scherer infers that, in the formation of granulite from gneiss, the rocks chiefly concerned have been the red and middle gneisses (upper and middle plutonites). The eruptive rock which has brought about the remelting and consequently dehydration of the gneiss—or which has been thrown up simultaneously with the granulites—cannot have been granite, although this rock traverses and intersects the whole granulite district in numerous veins. The remelting must, in fact, be assigned to a much later geological period, as indicated by the occurrence of the trap-granulites, i.e., especially of the gabbro and hypersthénite rocks. But whether any other eruptive rocks have taken part in the metamorphosis or not, the view—first advanced by Naumann from a purely geognostic standpoint—that the granulites themselves are eruptive rocks, is fully confirmed by their chemical constitution.

Analyses of the Saxon granulites have also been made by A. Stelzner (*Jahrbuch f. Mineralogie*, 1871, 244; *Chem. Soc. J.* [2], ix. 807), who regards them, not as eruptive, but as metamorphic rocks.

**GRAPES.** Researches on the ripening of grapes have been made by E. Pollucci (*Gazzetta chimica italiana*, ii. 392). A comparison of the amount of sugar and of acid in the external and internal portions of the flesh of the fruit, shows that the part nearest the centre contains more of the acid principle, and is, consequently, the last to ripen. During the ripening, the amount of sugar goes on increasing to a certain point, and then remains stationary, whilst the proportion of acid still continues to decrease, so that the grape must be considered to be ripe, not, as heretofore, when the amount of sugar ceases to increase, but rather when the acidity no longer diminishes.

**GRAPE-SUGAR.** See SUGAR.

**GREENSTONE** (Th. Petersen, *J. pr. Chem.* [2], vi. 197). The greenstones may be divided into two classes, viz.: (1.) The amphibolite or hornblende greenstones; (2.) The pyroxenic or augitic greenstones.

To the hornblende group belong diorite, with its varieties and congeners, the essential constituents of which are hornblende and a triclinic alkali-felspar. Sometimes also quartz is present, in which case the rock approximates to the trachytic series, and may even pass into syenite if it also contains orthoclase. The augitic greenstones are the true basic rocks. They all contain a plagioclasic alkali- or lime-felspar, but no quartz. They may be conveniently divided into two groups, the older and the younger.

The older division, which is developed chiefly in the transition formation, includes the rocks of the diabase family, to which belong: (*a.*) True diabase. (*b.*) Melaphyr and augitic porphyry, which contain true augite and are very much alike. (*c.*) Hypersthénite, containing ferruginous hypersthène, which, according to the recent investigations of Descloizeaux, crystallises in the rhombic system. (*d.*) Gabbro, containing comparatively light-coloured non-ferruginous enstatite, diallage, or smaragdite. All these rocks may be conveniently designated as 'true greenstones.'

To the later division of the augitic rocks belong those of the basaltic family: basalt, diorite, and basaltic lavas, for which, as proposed by Naumann, the collective name 'trap' may be retained.

The basic greenstones, and especially those containing augite, exhibit on the whole a considerable resemblance to one another, and their percentage composition is also nearly the same. The alkaline silicates are more variously developed in the basaltic than in the diabasic rocks, which latter do not contain glassy felspar, nepheline, &c. In the former, on the other hand, the augitic substance has in the course of ages been more or less altered and converted into chlorite. Titaniferous magnetic iron ore (in some cases also titaniferous iron), and in small quantity apatite, is common to both groups.

*The most important Constituents of the Basic Rocks.*—It has long been questioned whether any triclinic felspar is a regular constituent of diabbases. Petersen finds that oligoclase is usually present, whereas lime-felspar occurs in considerably smaller proportion, or is altogether wanting. In the younger greenstones, especially the basaltites, the oligoclase is sometimes replaced by orthoclase. Zeolites, mostly of comparatively recent formation, are diffused through all greenstones, especially the basaltites.

*Augite and Hornblende.*—The constitution of these minerals, and especially the part which alumina and ferric oxide play in them, has not yet been satisfactorily explained. Most of the analyses agree with the formula of a bisilicate, the excess of base which some of them exhibit being due to the iron, which is often present as magnetic oxide. Augite and hornblende sometimes occur together in greenstones, the augite, however, generally predominating.

*Chlorite.*—The constitution of minerals of the chlorite family is but imperfectly understood, the obscurity arising chiefly from the fact that they are products of the more or less advanced transformation of augitic minerals, and therefore difficult to obtain pure. Their mean composition is best expressed by Rammelsberg's formula  $2(3\text{RO} \cdot \text{SiO}_2) + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + 4\text{H}_2\text{O}$ . In the diabbases ferruginous chlorite is almost always present, the augite being sometimes completely converted into this mineral. It is often accompanied by a large quantity of finely-divided magnetic iron ore.

*Magnetic and Titaniferous Iron Ores.*—Magnetic iron oxide is a regular constituent of the basic rocks, both old and new, especially of the augitic greenstones. It often contains titanous acid. Titaniferous iron is of frequent occurrence in the dolerites. Titanic acid occurs in basic rocks, sometimes isolated, more frequently, however, as titaniferous iron.

*Apatite*, to the amount of several units per cent. is rarely absent from basic rocks, and is frequently met with in other rocks of plutonic origin, especially trachytes and lavas.

*Formation of Serpentine.*—Greenstones are not unfrequently serpentinised. Serpentine more or less distinctly stratified is often found amongst crystalline rocks, as gneiss, granite, diorite, gabbro, diabase, &c., but also nearest to those which contain a considerable quantity of magnesia. Silica and magnesia appear therefore to have a peculiar tendency to unite into a mass exhibiting the character of serpentine.

*The Greenstones as Matrices of useful Minerals and Ores.*—The beds of ore of Wittichen in Baden, appear to owe their existence to neighbouring hornblende slates containing nickel, cobalt, arsenic, bismuth, and silver. Many iron and copper ores, particularly the copper schist of Oberhessen, also the nickel and copper ores of the Dillenburg district, are probably derived from diabase. The origin of the important deposits of phosphorite in Nassau must also be assigned to diabase, which is everywhere rich in apatite.

**GUAIACUM.** E. Schaer (*Zeitschr. anal. Chem.* ix. 430) prepares tincture of guaiacum by dissolving 1 part of the recently pulverised resin in 100 parts of absolute alcohol, and keeps it in black glasses, in which it will remain unaltered for a long time.

The reaction of this tincture with copper salts in presence of hydrocyanic acid and with various cyanogen compounds of copper has been already noticed (p. 383). Schaer either pours the guaiacum tincture on the liquid to be tested, or mixes it with the latter till a strong opalescence is produced. In the former case a blue zone becoming continually broader makes its appearance at the surface of contact; in the latter the resinous precipitate assumes in a few minutes a light blue colour.

The true homologues of hydrocyanic acid, viz.: acetonitril, propionitril, capronitril, &c., produce a very distinct blueing, even when they have been completely freed from isocyanides or carbamides by repeated treatment with dilute hydrochloric acid. Of the carbamides, only the toluyl-compound was examined, which, whether in the state of liquid or of vapour, does not produce any blueing, either with tincture of guaiacum containing copper, or on guaiac paper moistened with a very weak solution of a copper salt. Schaer does not, however, infer from this that the entire group of carbamides is incapable of producing this reaction, inasmuch as the action of benzene derivatives may be much weaker than that of methyl-, ethyl-, or amyl-compounds. Normal sulphonyl compounds, as those of ethyl and amyl, blue the guaiac-copper solution as strongly

as their isomerides, the mustard-oils or sulphocarbimides. The blueing produced by these sulphocyanates, especially in the state of vapour, is much weaker than that developed by the normal cyanides. Methyl-, ethyl-, amyl-, and phenyl-sulphocarbimides behave in the same manner as ordinary mustard-oil. The amyl-compound, however, is distinguished from the rest by its much stronger action in the state of vapour. Phenyl-sulphocarbimide, on the other hand, exerts but a very feeble action, especially in the state of vapour.

Schönn (Zeitschr. anal. Chem. 1870, 209) observes that great care is necessary in the use of tincture of guaiacum for the detection of hydrocyanic acid, chromic acid, and ozone, inasmuch as the same effect may be produced by other substances. Guaiacum-paper moistened with solution of cupric sulphate is turned blue by ammonia, as well as by hydrocyanic acid. Tincture of guaiacum, in presence of sulphuric acid, is rendered blue, not only by chromic acid, but also by ferric chloride, potassium ferricyanide, gold chloride, potassium permanganate, molybdic acid, potassium nitrate, and potassium nitrite. Guaiacum resin assumes a blue colour with oxidising substances, and with potassium antimonate, barium carbonate and hydrochloric acid, lead acetate, calcium chloride, manganese chloride, copper nitroprusside, mercurous nitrate, and sodium sulphocyanate. Copper salts also colour tincture of guaiacum blue when very dilute. The reaction is more sensitive in presence of ammonium chloride, barium chloride, ammonium bromide, potassium iodide or cyanide, or ammonium fluoride.

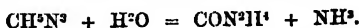
**GUANAPITE.** See GUANO.

**GUANIDINE**,  $\text{CH}_3\text{N}^+ = \text{C} \begin{Bmatrix} \text{NH}^2 \\ \text{NH} \\ \text{NH}^2 \end{Bmatrix}$ . Erlemmeyer obtained this base by the action

of cyanogen chloride on ammonia (i.e. of cyanamide on ammonium chloride, 1st Suppl. 654). According to Bannow (Deut. Chem. Ges. Ber. iv. 161) the chloride of cyanogen may be conveniently replaced by the iodide. The solubility of ammonium iodide in alcohol appears to hasten the formation of guanidine. Iodide of cyanogen with three times its weight of alcoholic ammonia (of 10 p.c.), heated in a sealed tube in the water-bath for three hours, gave almost the theoretical quantity of nearly pure guanidine salt. According to Ossikovsky, however (Bull. Soc. Chim. [2], xviii. 161), other products, including a volatile fatty acid are formed at the same time.

G. Bouchardat (Compt. rend. lxi. 961) by passing 150 litres of phosgene gas into ammonia, obtained, together with sal-ammoniac and urea, small quantities of guanidine, ammelide, and cyanuric acid.

Guanidine boiled with dilute sulphuric acid, or with baryta-water, assimilates the elements of water, and gives ammonia and urea, or the products of its decomposition.



**Substituted Guanidines.** *Dibenzyl-guanidine*,  $\text{CH}_2(\text{C}_6\text{H}_5)_2\text{N}^+ = \text{C} \begin{Bmatrix} \text{NH.C}_6\text{H}_5 \\ \text{NH} \\ \text{NH.C}_6\text{H}_5 \end{Bmatrix}$

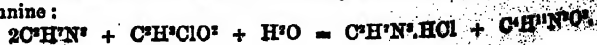
The hydrochloride of this base is formed by boiling an alcoholic solution of cyanbenzylamide (p. 182) with benzylamine hydrochloride, and the free base is formed by the action of dry cyanogen chloride on pure dry benzylamine. The hydrochloride crystallises in laminae melting at  $176^\circ$ , slightly soluble in water, more freely in alcohol. The *platinochloride* is crystalline. On adding caustic soda to a solution of the hydrochloride, dibenzylguanidine separates as an oil which soon solidifies, and crystallises from alcohol in colourless laminae or plates which melt at  $100^\circ$ , and dissolve freely in water, alcohol and ether (Strakosch, Deut. Chem. Ges. Ber. v. 692).

Phenyl-, tolyl-, and methyl-guanidine may be formed by the action of cyanamide on the hydrochlorides of aniline, toluidine, and methylamine respectively (Erlenmeyer, Deut. Chem. Ges. Ber. iii. 806); the last also by the action of methyl-cyanamide on ammonium chloride (Tawildarow, *ibid.* 477).

*Methyl-guanidine*,  $\text{CH}_3(\text{CH}_3)_2\text{N}^+ = \text{C} \begin{Bmatrix} \text{NH.CH}_3 \\ \text{NH} \\ \text{NH}^2 \end{Bmatrix}$ , appears to be identical with

methyluramine—which Dessaignes obtained by boiling an aqueous solution of creatine or creatinine with mercuric oxide (iii. 1009)—in every respect excepting in the form of its platinum salt, that of methyluramine crystallising, according to Sérarmont, in rhombohedrons, whereas, according to v. Kobell's measurements, that of methyl-guanidine crystallises in monoclinic forms (Erlenmeyer).

*Glycolyl-methyl-guanidine*,  $\text{C}_2\text{H}_4\text{N}^+\text{O}^2$ , is formed by the action of monochloroacetic acid at the boiling heat on methyl-guanidine, the action being analogous to that which the same acid exerts on triethylamine, triethylphosphine, piperidine, and strychnine:

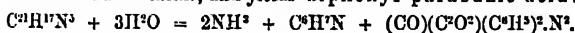


When an aqueous solution of chloracetate of methyl-guanidine is heated to 120°, the product boiled with lead hydrate, the lead precipitated by hydrogen sulphide, and the filtrate evaporated to a thin syrup, glycolyl-methyl-guanidine is obtained in colourless, thick, rhombic tablets, which soon agglomerate in irregular groups. These crystals are easily soluble in water, and are neutral to litmus-paper. When strongly heated they melt without subliming. Glycolyl-methyl-guanidine unites with gaseous hydrochloric acid, forming the salt  $C^4H^{11}N^3O^2.HCl$ , which cannot be prepared with the aqueous acid. With *platinic chloride* and *silver nitrate* it yields respectively the compounds  $C^4H^{11}N^3O^2.H^2PtCl^6$  and  $C^4H^{11}N^3O^2.Ag^2O$ . The hydrochloride melts below 100°, and if gaseous hydrochloric acid be passed over it at 100°, 2 mols. of the salt give up 1 mol. water, leaving the compound  $C^4H^{10}N^3O^2.2HCl$ .

*Triphenyl-guanidine*,  $C(C^6H^5)^3H^2N^3$ , is formed by the action of mercuric chloride on sulphocarbamide. When equal parts of these two substances in the dry state are heated together in an oil-bath to 140°–150°, the mass first melts, then froths and gives off hydrochloric and sulphydric acids. The fused mass, which smells like phenyl-sulphocarbamide, is lixiviated, first with boiling water and then with alcohol. The aqueous extracts, treated with soda-ley, yield yellow and white precipitates of triphenyl-guanidine, which, after recrystallisation from alcohol, melts at 145°. It crystallises in thin needles which, according to Groth's measurements, are rhombic six-sided prisms, having the axial ratio  $a : b : c = 0.6703 : 1 : 0.5575$  (H. L. Buff, *Deut. Chem. Ges. Ber.* ii. 498; *Zeitschr. f. Chem.* 1870, 54).

The alcoholic extract of the fused mass obtained in the above reaction yielded long, shining, strongly refractive needles of diphenylurea, melting at 235° and solidifying at 210°.

*Cyantriphenyl-guanidine*,  $C^3H^{11}N^5 = CH^2(C^6H^5)^3N^3.2CN$ , is formed, together with cyananiline, by the action of cyanogen on aniline. When purified it forms beautiful aurea-red crystals having a violet iridescence. Heated with dilute alcohol it gives off ammonia and aniline, and yields diphenyl-parabanic acid:



When its alcoholic solution is boiled with hydrochloric acid, the diphenyl-parabanic acid is likewise decomposed, the products being ammonia, aniline, carbon dioxide, and oxalic acid:



(Hofmann, *Deut. Chem. Ges. Ber.* iii. 763).

A compound isomeric with the above is obtained by the action of cyanogen on an alcoholic solution of triphenyl-guanidine. It forms yellowish-white crystals which, in contact with hydrochloric acid, turn red and are quickly resolved into ammonia and oxalyl-triphenyl-guanidine,  $C(C^6H^5)^3(C^2O^2)^2N^3$ . This latter, boiled with alcohol and hydrochloric acid, yields diphenyl-parabanic acid and its products of decomposition (Hofmann, *ibid.* 764).

*Naphthyl-diphenyl-guanidine*,  $C^2H^{10}N^3 = C(C^{10}H^7)(C^6H^5)^2H^2N^3$ .—When diphenyl-sulphocarbamide and naphthylamine in equal numbers of molecules are boiled in alcoholic solution with lead oxide till the whole of the sulphur is precipitated, the filtrate then evaporated, the residue dissolved in dilute hydrochloric acid, and concentrated hydrochloric acid added to the solution, *hydrochloride* of *naphthyl-diphenyl-guanidine* separates in indistinct crystals which form a crystalline double salt with platinic chloride. The *nitrate* is sparingly soluble. The free base forms crystalline crusts which melt at 155 (F. Tiemann, *Deut. Chem. Ges. Ber.* iii. 6; *Zeitschr. f. Chem.* [2], vi. 309).

*Naphthyl-tolyl-phenyl-guanidine*,  $C^4H^{12}N^3 = C(C^{10}H^7)(C^6H^5)(C^8H^7)H^2N^3$ , is prepared, like the preceding compounds, from phenyl-tolyl-sulphocarbamide and naphthylamine. In the free state it forms a clear, brittle resin, melting below 60°. The *nitrate* is sparingly soluble and crystalline; the *hydrochloride* is crystalline, and forms a sparingly soluble double salt with platinic chloride (Tiemann).

*Tetraphenyl-tolylene diguanidine*, or *Dicarbo-tetraphenyl-tolylene-hexamine*,  $C^8H^{12}N^6 = C^2(C^6H^5)^4(C^8H^7)^2H^4.N^6$ , is obtained in the manner above described from 2 mols. diphenyl-sulphocarbamide and 1 mol. tolylene-diamine. The free base forms a clear resin which melts at 76° and dissolves in chloroform, ether, alcohol, and benzene. The *platinichloride* has the composition  $C^8H^{12}N^6.2HCl$ ; the *nitrate* is sparingly soluble (Tiemann).

**GUANINE.** This base has been found in the excrement of a heron fed partly on fish, partly on flesh (Hoppe-Seyler, *Med.-Chem. Untersuchungen*, 1871, 582).

**GUANO.** According to Chevreul (*Compt. rend.* lxxvii. 463, 569, 901) the crystal-

lissable material dissolved from guano by cold water, consists mainly of ammonium oxalate mixed with yellow, red, and brown organic colouring matters. The residue left after complete extraction of guano with cold water yields avic acid to hot alcohol, although the residue originally possessed no smell of the acid. Prolonged washing does not remove the whole of the ammonium carbonate from the insoluble residue of guano. The bones of birds found in guano have entirely lost their cohesion, being reduced by trituration with water to orange flocks, the water at the same time becoming acid and dissolving some calcium phosphate. One example of guano yielded a salt containing calcium, ammonium, potassium, and oxalic acid, soluble in a little water, but decomposed by a larger quantity with precipitation of calcium oxalate. Chevreul concludes that these crystalline substances have been formed by a slow action in the absence of any notable proportion of water.

On the composition and properties of guano, see further, Chevreul (*Compt. rend.* lxxvi. 1376, 1500; lxxvii. 155; *Chem. Soc. J.* [2], xi. 1052; xii. 90).

*Guano from Malden Island.*—This guano is in the form of a coarse powder, of bright brown colour, and has the following composition:—

FeO <sup>s</sup>	K <sup>2</sup> O	Na <sup>2</sup> O	MgO	CaO	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	CO <sup>3</sup>	Cl	Sand	Organic matter	Water	N
·26	·28	1·71	1·86	43·51	37·58	·22	2·61	·82	·01	6·61	4·70	·29 = 100·40

It is similar to that from Baker Island, and is well adapted for the manufacture of superphosphate (J. Fittbogen, *Ann. d. Landwirthschaft, Wochenblatt*, 1872, 310).

*Minerals found in Guano.*—C. U. Shepard (*Sill. Am. J.* [2], i. 273) describes two new minerals—the homogeneity of which is perhaps doubtful—from the guano of Guanapo Island, north-east of the Chincha Islands, Peru. One of them, guanapite, occurs in nodules and veins, has a rhombic cleavage, and gives off ammonia in contact with the air. Hardness = 1·5; sp. gr. = 2·3. The other, guanoxalite, is a product of transformation of a bird's egg. It is milk-white, slightly translucent, has a nacreous lustre, and forms laminae with rhombic cleavage. Hardness less than 2; sp. gr. = 1·58. When heated it swells up, blackens, and melts, giving off a large quantity of ammonia, and leaving a white residue. The composition of these minerals is as follows:—

	Guanapite.	Guanoxalite.
Potassium sulphate . . . . .	67·75	40·20
Ammonium sulphate . . . . .	27·88	—
Ammonium oxalate . . . . .	3·75	29·25
Water . . . . .	—	30·46
	99·38	99·91

Shepard also enumerates five other minerals found in the vertebral column and the stomach of a bird imbedded in the guano, viz.: *Taylorite* (calcium oxalate), *Oxammite* (ammonium oxalate), *Phosphammite*, and *Diphosphammite* (ammonium phosphate in different stages of saturation).

**GUARANINE.** For the preparation of this substance from guarana, the following process is recommended by C. J. Williams (*Chem. News*, xxvi. 97). Finely-powdered guarana is mixed with one-third of its weight of hydrate of lime, and moistened with water. After an hour or two, it is placed in a drying closet, and completely dried at a moderate heat. It is then exhausted with boiling benzene, filtered, and the benzene distilled off. A small quantity of light-coloured oily matter is left, which is treated with boiling water, and again digested over a water-bath, until all traces of benzene have been dissipated, then filtered through a wetted filter so as to keep back the oil; the aqueous portion evaporated to a small bulk, and set aside for twenty-four hours, yields the guaranine white and pure, and requiring no further purification.

**GÜMBELITE.** A mineral occurring at Nordhalben, near Steben, in Upper Franconia, in thin fibrous layers on clay slate, or on the iron pyrites which occurs in small flattened masses. It is greyish-white, of a soapy to pearly lustre, translucent, soft, and pliant, and feels, when rubbed, like fine asbestos. It intumesces before the blow-pipe, and the fine fibres fuse into a mass resembling porcelain. It gives off water when heated, and resists the action of acids. Its analysis gave the following numbers:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	FeO	MgO	K <sup>2</sup> O	H <sup>2</sup> O	Undecomposed substance
50·62	31·64	3·00	1·88	3·18	7·00	1·46 = 98·05

(v. Kobell, *Jahrb. f. Mineralogie*, 1871, 174).



**GUM.** The compound obtained by heating gum-arabic to  $150^{\circ}$  with 2 parts of acetic anhydride, and regarded by Schützenberger & Naudin (*1st Suppl.* 658) as diacetyl-arabin,  $C^6H^4(C^2H^3O)^2O^2$ , appears from more recent experiments by Schützenberger (*Ann. Chim. Phys.* [4], xxi. 235) to be tetracetyl-diarabin,  $C^{12}H^{12}(C^2H^3O)^4O^{10}$ , inasmuch as the saturated acetyl derivative obtained by heating gum to  $180^{\circ}$  for five or six hours with 6 to 8 parts of acetic anhydride, has the composition  $C^{12}H^{12}(C^2H^3O)^4O^{10}$ . Both these acetyl-derivatives are white amorphous powders.

*Distinction of Gum-arabic from Dextrin.*—According to Hager (*Zeitschr. anal. Chem.* xi. 350) these bodies may be distinguished from one another by the following characters:

Gum contains no dextroglucose, which, however, is present in dextrin, and may be found by Trommsdorff's sugar-test.

Gum contains a lime-compound: hence its solution is rendered turbid and milky by oxalic acid, whilst a solution of dextrin remains almost clear.

Gum gives a slimy yellow deposit when its solution is mixed with a neutral ferric salt.

*Distinction between Gum-arabic and Sennar Gum.*—The presence of the cheaper Sennar gum in gum-arabic may be detected by dissolving 3 grams of the gum in 15 grams of cold distilled water, and adding 30 grams of basic lead acetate in several portions, with constant stirring and filtering. Pure gum-arabic filters easily, yielding in an hour 18 to 20 grams of scarcely opalescent filtrate, and leaving on the filter a residue which is no longer fluid. When 6 grams of the filtrate are mixed with 5 grams of water and  $1\frac{1}{2}$  gram of ammonia is added, the liquid remains almost clear. Gum-Sennar behaves in a similar manner. Sennar gum, on the other hand, gives a milky filtrate, and the filtration goes on for 24 hours till the filtrate weighs from 18 to 20 grams, after which the residue on the filter still appears fluid. When 6 grams of the filtrate clarified by a second filtration are diluted with 5 grams of water and mixed with the above specified quantity of ammonia, a white gelatinous mass is formed on agitation. By this character a mixture of the two kinds of gum may easily be recognised (Schlosser, *Chem. News*, xx. 120).

Gum mixed with dextrin exhibits the same characters as when mixed with Sennar gum; but dextrin solution alone is merely clouded by basic lead acetate, so that the smaller quantity of the precipitate produced by this reagent, is sufficient of itself to indicate the presence of dextrin. Characteristic of dextrin also is the peculiar smell of bread which is emitted on dissolving it in hot water (Schlosser).

*Estimation and Separation of Gum and Dextrin.* (J. Roussin, *J. Pharm.* [4], vii. 251).—These substances may be separated by means of ferric chloride, which precipitates the gum and not the dextrin. The liquid containing them is evaporated to a syrup, mixed with 10 times its volume of 90 p. c. spirit, and the resulting precipitate is washed with spirit of the same strength and dried. One gram of the residue is then dissolved in 10 c. c. of water; the solution is mixed with 30 c. c. spirit of 56 p. c., 4 drops of ferric chloride solution (containing 25 p. c. of the anhydrous chloride) and a few decigrams of pounded chalk; and after stirring briskly and leaving the liquid at rest for three or four minutes, the whole is thrown on a filter. The precipitate is washed with spirit of 56 p. c. and from the filtrate the dextrin is precipitated by spirit of 90, or better 95 p. c. After 24 hours the alcoholic liquid is decanted, and the dextrin is dissolved in a small quantity of water, then dried on the water-bath and weighed. The compound of gum with ferric chloride must be dissolved in dilute hydrochloric acid, the gum separated by precipitation with alcohol of 95 p. c. and after washing likewise dissolved in water, dried and weighed.

The precipitation of gum from the slightly alcoholic liquid by ferric chloride with addition of chalk is so complete that nothing but calcium chloride can be found in the filtrate. On the other hand, the precipitate of ferric oxide separated from pure dextrin solutions, does not contain a trace of dextrin, the whole of that substance being found in the filtrate. If a precipitate is formed on addition of ferric chloride alone the presence of gum is demonstrated; the clouding of the filtrate by addition of 8 or 10 times its volume of 90 p. c. spirit indicates the presence of dextrin.

**GUMMIC ACID.** A. Claus (*J. pr. Chem.* [2], iv. 63) in continuing his examination of the products of decomposition of grapo-sugar by potash in alkaline solution (*1st Suppl.* 659), has arrived at the somewhat modified view that the acid obtained by Reichardt from the so-called gummates (ii. 956) was a mixture of tartaric acid with several other syrupy or difficultly crystallisable acids, while the crystallised acid analysed by Reichardt, was tolerably pure tartaric acid, which had separated in small quantity from the evaporated mixture of acids.

**GUNPOWDER.** Important researches on the products of combustion of gun-

powder fired under circumstances similar to those which exist when it is exploded in guns or mines have recently been published by Captain Noble and Mr. F. A. Abel.

The gunpowder used in the experiments included five kinds, viz. pebble powder, rifle large-grain (cannon) powder, fine-grain powder, and rifle fine-grain powder (all of Waltham-Abbey manufacture), and also a spherical pellet powder of Spanish manufacture, specially selected for experiment as presenting considerable difference in composition from the English powders. The composition of these powders is shown in the following Table:—

TABLE I.  
*Results of Analysis of Gunpowders employed.*

Components, per cent.	Description of Gunpowders employed in Experiments				
	Pebble powder  Waltham Abbey	Rifle Large-grain  Waltham Abbey	Rifle Fine-grain  Waltham Abbey	Fine-grain  Waltham Abbey	Spanish Spherical Pebble powder
Saltpetre . . .	74.67	74.95	75.04	73.55	75.30
Potassium sulphate . . .	0.09	0.15	0.14	0.36	0.27
Potassium chloride . . .	—	—	—	—	0.02
Sulphur . . .	10.07	10.27	9.93	10.02	12.42
Char- coal { Carbon . . .	12.12	10.86	10.67	11.36	8.65
Hydrogen . . .	0.42	0.42	0.52	0.49	0.38
Oxygen . . .	1.45	1.99	2.66	2.57	1.68
Ash . . .	0.23	0.25	0.24	0.17	0.63
Water . . .	0.95	1.11	0.80	1.48	0.65

The apparatus consisted of a mild steel vessel, of great strength, carefully tempered in oil, in the chamber of which the charge to be exploded was placed. The main orifice of the chamber was closed by a screwed plug, called the firing-plug, fitted and ground into its place with great exactness. In the firing-plug itself was a conical hole, stopped by a plug, also ground into its place with great accuracy, and for purposes of insulation, covered with the finest tissue-paper. Two wires (one in the insulated cone, the other in the plug) were inserted, and joined by a very fine platinum wire passing through a small glass tube filled with mealed powder. By completing connection with a Daniell's battery, the charge could be fired.

There were two other apertures in the chamber—one communicating with the arrangement for letting the gases escape, the other containing the crusher-apparatus for determining the tension at the moment of explosion.

The pressures actually observed with this apparatus varied from over 36 tons on the square inch to about 1 ton on the square inch.

On opening the explosion-vessel after the gases had been allowed to escape, the solid products were found collected at the bottom in a hard compact mass extremely difficult to remove, there being generally an exceedingly thin (in fact, with large charges, quite an inappreciable) deposit on the sides.

The surface of the deposit was generally perfectly smooth and of a very dark grey, almost black, colour. This colour, however, was only superficial, and through the black could be perceived what was probably the real colour of the surface, a dark olive-green. The surface of the deposit and the sides of the cylinders had a somewhat greasy appearance, and were indeed greasy to the touch.

The deposit always smelt powerfully of sulphuretted hydrogen, and often strongly of ammonia. It was always exceedingly deliquescent, and after a short exposure to the air became black on the surface, gradually passing over into an inky-looking pasty mass.

As regards the proportions of total solid and gaseous products furnished by the several powders, remarkable uniformity was exhibited by the results of explosion of the same powder at different pressures, and no very considerable difference existed between the proportions furnished by the three powders chiefly used in the researches. The largest grain, or pebble powder, yielded most gas; the quantity furnished by R.L.G. powder was not greatly inferior, but was decidedly more considerable than that yielded by the smallest powder (F.G.).

The composition of the gas furnished by the explosion of all the English powders

was throughout remarkably uniform, but presented certain apparently well-defined small variations, regulated by the pressure under which the products were developed, the chief being a steady increase in the proportion of carbonic anhydride, and decrease in that of carbonic oxide, in proportion as the pressure was increased. The composition of the *solid* products exhibited much greater variations, chiefly in regard to the state of combination in which the sulphur existed. These variations were exhibited, not merely by the products obtained from the different powders, but also, and to as great an extent, by those which one and the same powder furnished at different pressures, and apparently without reference to the pressure, excepting in the case of the very lowest (the powder occupying 10 per cent. of the total space in the chamber).

The reactions which occur among the powder-constituents, in addition to those which result in the development of gas of fairly uniform composition (and very uniform as regards the proportions which it bears to the solid), from powders not differing widely in constitution from each other, are susceptible of very considerable variations, regarding the causes of which it appears only possible to form conjectures. Any attempt to express, even in a comparatively complicated chemical equation, the nature of the metamorphosis which a gunpowder of average composition may be considered to undergo when exploded in a confined space, would therefore only be calculated to convey an erroneous impression as to the simplicity or the definite nature of the chemical results, and their uniformity under different conditions, while it would in reality possess no important bearing upon the elucidation of the theory of explosion of gunpowder. But the experiments under consideration show decidedly that the chemical theory of the decomposition of gunpowder, as based upon the results of Bunsen *et al.* Schischkoff, and accepted in recent text-books, is as far from representing the general metamorphosis of gunpowder as was the old and long-accepted theory, according to which the primary products were simply potassium sulphide, carbonic anhydride, and nitrogen.

The principal results of the investigation are summarized as follows, and for convenience are computed upon 1 gram of powder, occupying 1 c.c. :—

(a) *First, with regard to powder fired in a close vessel.*

1. On explosion, the products of combustion consist of about 57 hundredths by weight of matter which ultimately assumes the solid form, and 43 hundredths by weight of permanent gases.
2. At the moment of explosion, the fluid products of combustion, doubtless in a very finely divided state, occupy a volume of about 0.6 c.c.
3. At the same instant the permanent gases occupy a volume of 0.4 c.c., so that both the fluid and gaseous matter are of approximately the same specific gravity.
4. The permanent gases generated by the explosion of a gram of powder are such that, at 0° C. and 760 mm. barometric pressure, they occupy about 280 c.c., and therefore about 280 times the volume of the original powder.
5. The constituents of the solid and gaseous products are as shown in Tables II. and III. :—

TABLE II.

*Showing illustrative Examples of the Analytical Results obtained.*

	Pebble		R.L.G.		F.G.	
Pressure of explosion in tons per square inch	1.4	12.5	1.6	35.6	3.7	18.2
Percentage weight of solid products	50.12	55.17	57.22	57.14	58.17	58.09
Percentage weight of gaseous products	43.88	44.83	42.78	42.86	41.83	41.92
Percentage weights of solid products of explosion :—						
Potassium carbonate	55.50	56.15	52.56	65.71	59.39	43.00
" sulphate	15.02	11.03	20.47	8.52	24.22	21.00
" thiosulphate	20.73	6.13	20.37	8.59	5.30	32.07
" monosulphide	7.41	19.12	4.02	7.23	5.12	—
" sulphocyanate	0.09	0.23	trace	0.36	0.02	0.23
" nitrate	0.48	3.20	0.56	0.19	0.08	0.19
" oxide	—	—	—	—	—	2.98
Ammonium sesquicarbonate	0.16	0.08	0.06	0.18	0.15	0.03
Sulphur	0.61	0.17	1.25	9.22	5.72	0.47
Carbon	trace	trace	0.71	—	trace	trace

## GUNPOWDER.

TABLE II (continued).

Percentage volumes of gaseous products:—

	Pebble		R.L.G.		F.G.	
Carbonic anhydride . . . . .	46.66	49.82	48.99	51.79	47.41	53.02
Carbonic oxide . . . . .	14.76	13.36	8.98	8.32	12.35	7.91
Nitrogen . . . . .	32.75	32.19	35.60	34.64	32.35	34.20
Sulphhydric acid . . . . .	3.13	1.96	4.06	2.61	3.76	2.03
Marsh-gas . . . . .	—	0.58	0.29	0.41	—	0.50
Hydrogen . . . . .	2.70	2.08	2.07	2.04	4.13	2.13
Oxygen . . . . .	—	—	—	0.18	—	0.16

TABLE III.

Showing the Composition by Weight of the Products of Explosion of a Gram of Powder as furnished by the above Examples.

	Pebble		R.L.G.		F.G.	
	gram	gram	gram	gram	gram	gram
Potassium carbonate . . . . .	.3115	.3098	.3067	.3755	.3484	.2499
„ thiosulphate . . . . .	.1163	.0338	.1166	.0491	.0308	.1863
„ sulphate . . . . .	.0843	.0658	.1171	.0487	.1409	.1220
„ sulphide . . . . .	.0416	.1055	.0230	.0413	.0298	—
„ sulphocyanate . . . . .	.0005	.0013	.0000	.0021	.0001	.0013
„ nitrate . . . . .	.0027	.0011	.0032	.0011	.0005	.0011
„ oxide . . . . .	—	—	—	—	—	.0173
Ammonium sesquicarbonate . . . . .	.0009	.0004	.0003	.0009	.0009	.0002
„ carbon . . . . .	—	—	.0072	—	—	—
„ sulphur . . . . .	.0034	.0340	.0041	.0527	.0333	.0027
Total solid . . . . .	.5612	.5517	.5722	.5714	.5817	.5808
Sulphhydric acid . . . . .	.0134	.0084	.0166	.0077	.0154	.0081
Oxygen . . . . .	—	—	—	—	—	.0006
Carbonic oxide . . . . .	.0519	.0473	.0303	.0356	.0416	.0268
Carbonic anhydride . . . . .	.2577	.2770	.2597	.2750	.2512	.2718
Marsh-gas . . . . .	—	.0012	.0006	.0015	—	.0009
Hydrogen . . . . .	.0007	.0005	.0005	.0003	.0010	.0005
Nitrogen . . . . .	.1151	.1139	.1201	.1085	.1091	.1117
Total gaseous . . . . .	.4388	.4483	.4278	.4286	.4183	.4192

6. The tension of the products of combustion, when the powder fills entirely the space in which it is fired, is about 6,400 atmospheres, or about 42 tons per square inch.

7. The tension varies with the mean density of the products of combustion, according to the law given in the equation:

$$p = \text{const.} \times \frac{\delta}{1 - \alpha \delta} \quad (1)$$

where  $\alpha$  is a constant determined from the experiments. The close agreement of the results of calculation from this form and those of experiment, is shown in the following Table:—

TABLE IV.

Showing the comparison, in tons per square inch, between the pressures actually observed in a close vessel and those calculated from the formula (1).

Density of products of combustion	Value of $p$ deduced from direct observation	Value of $p$ deduced from equation (1) $\alpha = .65$	Density of products of combustion	Value of $p$ deduced from direct observation	Value of $p$ deduced from equation (1) $\alpha = .65$
	Tons per square inch	Tons per square inch		Tons per square inch	Tons per square inch
.10	1.47	1.56	.60	14.30	14.59
.20	3.26	3.36	.70	19.09	18.79
.30	5.33	5.45	.80	25.03	24.88
.40	7.75	7.91	.90	32.46	31.73
.50	10.69	10.84	1.00	41.70	41.70

8. About 705 gram-units of heat are developed by the decomposition of 1 gram of powder, such as used in the experiments.

9. The temperature of explosion is about  $2200^{\circ}$  C.

(b) *When powder is fired in the bore of a gun.*

1. The products of explosion, at all events as far as regards the proportions of total solid and gaseous matters, are the same as in the case of powder fired in a close vessel.

2. The work on the projectile is effected by the elastic force due to the permanent gases.

3. The reduction of temperature and pressure due to the expansion of the permanent gases is in a great measure compensated by the heat stored up in the liquid residue.

4. The law connecting the tension of the products of explosion with the volume they occupy is stated in the equation :

$$p = p_0 \left\{ \frac{v_0(1-\alpha)}{v-\alpha v_0} \right\}^{\frac{c_p + \beta\lambda}{c_v + \beta\lambda}}; \quad . \quad . \quad . \quad (2)$$

in which  $p$  denotes the tension and  $v$  the volume of the products of explosion;  $\alpha$  the proportion occupied by the solid products;  $c_v$  and  $c_p$  the specific heats of the permanent gases at constant temperature and pressure;  $\lambda$  the mean specific heat of the non-gaseous products;  $\beta$  the ratio between the weights of the gaseous and non-gaseous portions of the charge.

5. The work that gunpowder is capable of performing in expanding in a vessel impervious to heat is given by the equation :

$$W = \frac{p_0 v_0 (1-\alpha) (C_p + \beta\lambda)}{C_p - C_v} \left\{ 1 - \left( \frac{v_0(1-\alpha)}{v-\alpha v_0} \right)^{\frac{c_p - c_v}{c_v + \beta\lambda}} \right\}. \quad . \quad . \quad (3)$$

and the temperature during expansion by the equation :

$$t = t_0 \left( \frac{v_0(1-\alpha)}{v-\alpha v_0} \right)^{\frac{c_p - c_v}{c_v + \beta\lambda}}. \quad . \quad . \quad . \quad (4)$$

6. The total theoretic work of gunpowder, when indefinitely expanded, is about 332,000 gram-met. per gram of powder, or 486 foot-tons per lb. of powder.

With regard to one or two other points to which attention was specially directed, the results appear to warrant the following conclusions :—

1. Very small-grain powders, such as F. G. and R. F. G., furnish very decidedly smaller proportions of gaseous products than a large-grain powder (R. L. G.); while the latter, again, furnishes somewhat smaller proportions than a still larger powder (pebble), though the difference between the total gaseous products of these two powders is comparatively inconsiderable.

2. The variations in the composition of the products of explosion furnished, in close chambers, by one and the same powder under *different* conditions as regards pressure, and by two powders of similar composition under the *same* conditions as regards pressure, are so considerable, that no value whatever can be attached to any attempt to give a general chemical expression to the metamorphosis of a gunpowder of normal composition.

3. The proportions in which the several constituents of solid powder-residue are formed are quite as much affected by slight accidental variations in the conditions which attend the explosion of one and the same powder in different experiments, as by decided differences in the composition as well as in the size of grain of different powders.

4. In all but very exceptional results, the solid residue furnished by the explosion of gunpowder contains, as important constituents, potassium carbonate, sulphate, thio-sulphate, and sulphide, the proportion of carbonate being very much higher, and that of sulphate very much lower, than stated by recent investigators.

**GYPSUM.** Schott (*Dingl. pol. J.* cxvii. 357) has examined the reaction of gypsum with potassium sulphate. In the first place he has verified the previously observed fact, that even unburnt gypsum, when mixed with solutions of certain salts, especially potassium sulphate, hardens like burnt gypsum with water. Equal parts by weight (corresponding with equal numbers of molecules) of pulverised selenite and potassium sulphate solidify, when made into a paste with water, more quickly than burnt gypsum with water. A hardening, though slower, may also be observed when only  $\frac{1}{10}$  mol. potassium sulphate is mixed with 1 mol. gypsum. The hardening of burnt gypsum is very much accelerated by the addition of potassium sulphate to the water used. When the two salts are mixed in molecular proportions, and stirred up with a small quantity of water, the mixture solidifies before it can be poured out of the vessel.

With equal weights of water and the mixture of salts just mentioned, a paste is obtained which may be poured out just before it solidifies, and in solidifying exudes crusts of potassium sulphate. Burnt gypsum, mixed with a cold-saturated solution of potassium sulphate, solidifies instantly, and the mixture cannot be poured out of the vessel if the weight of the solution is less than about double of that of the gypsum. If the quantity of water is greater, the mixtures solidify more slowly, always, however, more quickly than gypsum with water. The casts become curved in solidifying. When burnt gypsum is mixed with a solution of potassium sulphate saturated at the boiling heat, the mixture can scarcely be completed before solidification takes place. The casts made with gypsum and potassium sulphate are not more compact than those made with water, since a large quantity of water is required to make a mixture that will pour out, and this makes the solidified masses of looser texture. But the casts obtained with potassium sulphate solution have a nacreous and satiny lustre, and are altogether handsomer than the chalky products obtained with gypsum and water.

Schott confirms the suggestion of L. Gmelin that double sulphates of calcium and potassium are formed in this process. When pulverised selenite is added to a solution of potassium sulphate, and the liquid quickly stirred and filtered, the filtrate deposits satiny laminae having the composition  $\text{CaSO}_4 \cdot \text{K}^2\text{SO}_4 \cdot \text{H}_2\text{O}$ .

Potassium carbonate, stirred up with gypsum and water, produces potassium sulphate, which then acts as above. Sodium sulphate does not produce the same effect.

A solution of cream of tartar does not bring about the solidification of unburnt gypsum, but burnt gypsum mixed with the same solution hardens very quickly. The formation of the above-mentioned double salt, however, does not appear to take place, the casts being merely mixtures of gypsum and crystals of cream of tartar.

On crystals of gypsum from various localities, see *Jahrbuch für Mineralogie*, 1871, 572, 881; *Jahresb. f. Chem.* 1869, 1240; 1870, 1328; 1871, 1180.

*Gypsum as a Fertiliser.*—The power of gypsum to augment the fertility of soils may doubtless be ascribed in great measure to its property of facilitating the decomposition of complex rocks containing alkaline silicates, and thereby bringing the alkalis into a condition favourable to their ready absorption by the roots of plants.

To estimate the intensity of this decomposing action, A. Cossa (*Gazzetta chimica italiana*, iii. 185) has compared the quantity of matter dissolved, in a given time and within given ranges of temperature, from various rocks, by a saturated solution of gypsum, with the quantities dissolved out of the same rocks under similar conditions by pure distilled water. He finds that 1,000 parts of pure water dissolve 2.19 parts of pure crystallised gypsum at  $16^\circ\text{--}25$  and 2.352 at  $22^\circ$ , numbers agreeing nearly with those obtained by other experimenters.

The rocks were reduced to very fine powder, and left for twenty days in contact with a saturated solution of gypsum at temperatures ranging from  $16^\circ$  to  $22^\circ$ . The results are given in the following Table, together with those obtained in like manner with pure water:—

	Matter dissolved out	
	By pure water	By a saturated solution of gypsum
	Per cent.	Per cent.
Gneiss, containing undecomposed orthoclase and potash mica	0.125	0.463
Trachyte, decomposing, from Monte Chioja, Vicenza	0.0937	0.2562
Trachyte, undecomposed, from Monte Ortona (Euganian Hills)	0.0871	0.138
Trachyte, porphyroidal, decomposing (containing sanidine, mica, hornblende), from San Pietro	0.0567	0.0927
Montagnone (Euganian Hills)		0.1630
Trachyte from San Daniele	0.0750	
Granite (albite, quartz, mica), from Montorfano, Lago Maggiore	0.0727	0.207
Granite (orthoclase, mica containing a trace of lithia, quartz), from Baveno, Lago Maggiore	0.0990	0.2875
Felspar, white, compact, in veins in Diorite: from Mosso, Biella	0.350	0.714
Basalt, compact, of Monte Nuova (Euganian Hills)	0.1271	0.394
Perlite, from Monte Sieva (Euganian Hills)	0.0624	0.1963

The solvent action exercised by gypsum on rocks containing alkaline silicates may perhaps give rise to the presence of potash, soda, and lithia in certain mineral waters, especially in sulphuretted waters.

## H.

**HÆMATEIN.** See HÆMATOXYLIN.

**HÆMATIN,**

**HÆMATOLIN,**

**HÆMATOPORPHYRIN,**

} See BLOOD (p. 201).

**HÆMATOXYLIN**,  $C^{16}H^{10}O^8 = C^{16}H^8(OH)^8$  (F. Reim, *Deut. Chem. Ges. Ber.* iv. 329). This compound, treated with oxidising agents, yields nothing but oxalic acid; and it does not form any nitro-derivatives. With chlorine, bromine, phosphorus pentachloride, potassium chlorate and hydrochloric acid, and with hydriodic or hydrobromic acid, it yields only resinous products not admitting of purification. Treated with sodium-amalgam, or with zinc and sulphuric acid, it does not take up hydrogen. Heated with zinc-dust, it yields only a very small quantity of a crystallisable body suspended in an oily liquid.

*Acetyl chloride* acts easily on hæmatoxylin; and on evaporating the product over the water-bath, pouring the remaining syrupy mass into water, quickly collecting the curdy precipitate on a filter, and dissolving it, after washing, in gently heated alcohol or in acetic acid, the solution on cooling deposits the hexacetyl-compound,  $C^{16}H^8(C^2H^3O)^6O^8$ , in the form of extremely fine, soft, silky, crystalline tufts which, after pressing, may be kept without sensible alteration, but become coloured on exposure to the air when moist. This compound may be dried at  $100^\circ$  without decomposition. A similar substitution-product is formed with *benzoyl chloride*.

When an ethereal solution of hæmatoxylin is mixed with a few drops of strong nitric acid, hæmatein,  $C^{16}H^{12}O^8 \cdot 3H^2O$  (iii. 1), separates in small brown-red tufts of crystals, which give off 2 mols. water over oil of vitriol and the whole when heated to  $130^\circ$ . By boiling it with zinc and sulphuric acid, or better with sulphurous acid, till it is decolorised, it is reconverted into hæmatoxylin.

Hæmatoxylin fused with potash yields pyrogallic acid. This reaction shows that it belongs to the aromatic group, and the formation of its hexacetyl and hexbenzoyl derivatives shows that it contains six hydroxyl groups.

**HÆMOCHROMOGEN.** See BLOOD (p. 202).

**HÆMOGLOBIN.** See BLOOD (p. 198). Observations on the variations in the amount of hæmoglobin in the blood according to the age of the animal and its position in the zoological series have been made by Quinquaud (*Consp. rend.* lxxvii. 487). He finds that—

1. The progressive diminution in the amount of hæmoglobin contained in equal volumes of the blood, follows, as a rule, the steps of the animal scale.

2. The blood of young animals contains less hæmoglobin than that of adults. The amount decreases slightly during the first few days of extra-uterine life, rises during childhood, remains stationary during adult life, and finally falls slowly during old age.

3. The blood of birds is much less rich in hæmoglobin than that of mammals, but the weight of the globules is rather greater in the former than in the latter, though the mammalian globules contain only a third of the quantity of albuminous material present in those of birds.

4. As a rule, the females have less hæmoglobin than the males.

5. The lymph of crustaceans contains 4 to 5 cubic centimeters of oxygen in 100, whereas ordinary water in the middle of winter, when completely saturated, contains only 1 cubic centimeter in 100.

Quinquaud also finds that there is an exact relation between the quantity of oxygen which blood can absorb and the amount of hæmoglobin it contains, so that the latter can be determined by ascertaining the former. The quantity of oxygen absorbed by 100 cubic centimeters of human blood is 260 c.c., of ox-blood 240 c.c., and of duck's

blood 170 c.c. The quantities of iron in 1,000 grams of these kinds of blood are 0.53, 0.48, and 0.34 grm. respectively. According to Hoppe-Seyler's computation, that 0.43 grm. of iron corresponds with 100 grams of hæmoglobin, the quantities of this substance in 1,000 grams of these kinds of blood are 125, 120, and 52 grams respectively. The numbers obtained by Preyer from observations with the spectroscopes are a little higher, but bear the same proportions. The amount of hæmoglobin in the blood of the fowl is nearly the same as in that of the duck (*Compt. rend.* lxxi. 1486).

**HALLOYSITE** (iii. 6). A specimen of this mineral from Elba analysed by A. d'Achiardi (*Sill. Am. J.* [4], xlix. 402) was found to contain:

SiO <sup>2</sup>	AlF <sup>2</sup>	MgO	CaO	K <sup>2</sup> O	H <sup>2</sup> O
55.15	27.72	5.10		1.15	10.20 = 99.32.

It is milk-white with black and flesh-coloured spots, opaque, but becomes translucent when immersed in water.

**HALOGENS, OXYGEN-ACIDS** of (Kümmerer, *Pogg. Ann.* cxxxviii. 390). Kümmerer proposes to designate these acids, together with hydrochloric acid, as follows:—

Cl	.	.	.	Chlorine
ClH	.	.	.	Chloric acid (Hydrochloric acid)
ClHO	.	.	.	Oxychloric (Hypochlorous) acid
ClHO <sup>2</sup>	.	.	.	Dioxychloric acid
ClHO <sup>3</sup>	.	.	.	Trioxychloric (Chloric) acid
ClHO <sup>4</sup>	.	.	.	Tetroxychloric (Perchloric) acid.

Similar names are given to the acids of bromine and iodine.

**Bromic (Trioxylbromic) Acid, BrHO<sup>3</sup>.** According to Henry, potassium bromide is converted into bromate by fusion with the chlorate. Rammelsberg did not succeed in obtaining the bromate by this process. Kümmerer, on the other hand, finds that the formation of the bromate really takes place, but that on account of the decomposibility of the salt it is not easy to carry the process to a successful issue. The best result was obtained by fusing 10 grams of potassium chlorate in a porcelain crucible at the lowest possible temperature and adding, with stirring, the calculated quantity (or better, rather less) of potassium bromide by small portions at a time, and heating till the mass had become pasty and began to give off large bubbles. Many experiments failed, however, in spite of all precautions, and the yield was always below the calculated amount. Addition of potassium hydrate or sodium carbonate, and the use of sodium bromide or barium bromide, did not improve the result. The potassium bromate may be obtained pure by repeated crystallisation from water. A better and surer method of preparing it is by the action of bromine on chloric acid or its potassium salt. Chlorine is passed into a solution of potassium carbonate (6K<sup>2</sup>CO<sup>3</sup>) till effervescence begins, and bromine (2Br) is then added. The hypochlorous acid formed in the first instance serves to oxidise the bromine:—



and the chlorine thereby set free acts on the still undecomposed potassium carbonate, again producing chloric acid, carbon dioxide, and potassium chloride. To prepare free bromic acid HBrO<sup>3</sup>, either a slow stream of hypochlorous anhydride, Cl<sup>2</sup>O, is passed into bromine under water, or bromine is added to silver bromate suspended in water till it no longer disappears. The acid obtained by this latter process is quite pure. Evaporated in an open dish till decomposition began (formation of bromine and free oxygen), it exhibited a strength of 4.26 p.c. HBrO<sup>3</sup>. On distilling it in a retort, the distillate mostly exhibited an amount of oxygen somewhat less in proportion to the bromine than that required by the formula HBrO<sup>3</sup>. It appears, therefore, that bromic acid is not volatile under ordinary pressures, but splits up, on distillation, like chloric acid, probably yielding a lower oxygen-compound of bromine, which is perhaps resolved, by prolonged contact with water, into bromic acid and bromine, or hydrobromic acid. The boiling points of the several solutions of the acid could not be determined, on account of its great tendency to decompose; the thermometer, however, never rose above 100°. When concentrated in a vacuum till it begins to decompose, it contains 50.50 p.c. HBrO<sup>3</sup>, corresponding exactly with the formula HBrO<sup>3</sup> + 7H<sup>2</sup>O.

**Chloric (Trioxylchloric) Acid, HClO<sup>3</sup>.**—The aqueous solution of this acid likewise exhibits, when concentrated in a vacuum, the composition HClO<sup>3</sup> + 7H<sup>2</sup>O. The



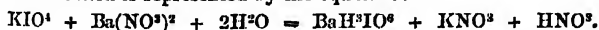
specific gravity of this hydrate at 14.2° is 1.282. If left longer in the vacuum over sulphuric acid, it finally attains a degree of concentration at which tumultuous evolution of gas takes place. Just before this point is attained the liquid has the composition  $2\text{HClO}^3 + 9\text{H}^2\text{O}$ .

*Iodic (Trioxiodic) Acid,  $\text{HIO}^3$* , was prepared by decomposing its silver salt\* with iodine, as the acid separated from the barium salt by dilute sulphuric acid always contains either barium or sulphuric acid. All solutions of this acid, the most concentrated as well as the most dilute, were found to boil exactly at 100°. At 13° one part of water dissolves 1.874 pt.,  $\text{I}^2\text{O}^5$ . This solution is viscid, cannot be filtered through paper, on which indeed it acts like strong sulphuric acid, converting it into a kind of vegetable parchment. It crystallises at -17°, apparently in hexagonal plates, melts constantly at -15°, and has the composition  $2\text{HIO}^3 + 6\text{H}^2\text{O}$ , analogous to that of the second hydrate of chloric acid; sp. gr. = 2.1269 at 13°. The anhydride,  $\text{I}^2\text{O}^5$ , has a specific gravity of 4.7987 at 9°; Millhol found it to be 4.250. According to Kämmerer's number, the atomic volume is 69.60. Further determinations of specific gravity showed that the atomic volumes of the corresponding hydrates of chloric and iodic acid are equal.

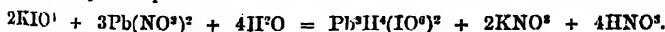
Formula of the Hydrate	Amount of Anhydride per cent.	Atomic Weight	Specific Gravity	Atomic Volume
$\text{HClO}^3 + 7\text{H}^2\text{O}$	35.73	210.5	1.262	166.7
$\text{HIO}^3 + 7\text{H}^2\text{O}$	55.30	304	1.8256	165.4
$\text{HClO}^3 + 15\text{H}^2\text{O}$	21.29	351.5	1.161	305.2
$\text{HIO}^3 + 15\text{H}^2\text{O}$	37.44	446	1.486	200.5
$\text{HClO}^3 + 20\text{H}^2\text{O}$	16.98	444.5	1.128	394.2
$\text{HIO}^3 + 20\text{H}^2\text{O}$	31.16	536.0	1.389	391.6

The corresponding solutions of the hydrogen-compounds did not exhibit this relation.

*Periodic (Tetra-oxiodic) Acid,  $\text{HIO}^4$* .—When a hot aqueous solution of the salt,  $\text{KIO}^4$ , is mixed with a hot solution of barium nitrate, and the mixture heated for a short time, no precipitate is formed, even after cooling, but the liquid exhibits a strong acid reaction. If, however, the acid solution be mixed with an equivalent quantity of potassium or sodium acetate, a precipitate is immediately formed, perfectly amorphous and not quite insoluble in water. This precipitate has the composition of Langlois' salt,  $\text{BaH}^2\text{IO}^6$ , and not that assigned to it by Rammelsberg, viz.,  $\text{Ba}^2\text{I}^2\text{O}^9 + 34\text{H}^2\text{O}$ . Its formation is represented by the equation:—



This salt is not decomposed either by the carbonate or the sulphate of potassium or ammonium. The reaction between potassium periodate and lead nitrate takes place as represented by the equation—



In preparing the acid,  $\text{HIO}^4$ , from the brown silver salt, it is better to decompose this salt with chlorine or bromine than with nitric acid.

The polybasicity of periodic acid shows that iodine must be a polyatomic element, since, if it is regarded as only monatomic, the acid in question must be represented by the formula  $\text{I}-\text{O}-\text{O}-\text{O}-\text{O}-\text{H}$ , which is that of a monobasic acid.

*Relations of Affinity of the Halogen Elements in their Oxygen-compounds.*—The order of affinity of the three elements, chlorine, bromine, and iodine, is not the same in their oxygen-compounds as in their hydrogen-compounds. In the latter, as is well known, chlorine is displaced by bromine, and bromine by chlorine; in the oxygen-compounds, on the other hand, chloric acid, for example, chlorine is displaced by iodine. To throw further light on these relations, Kämmerer has studied the following reactions:—

- Br on  $\text{HClO}$  . . . this action has been already described.
- Br on  $\text{HClO}^2$  . . . no action in aqueous solution.
- Br on  $\text{ClO}^2$  . . . no action, even in presence of water,

This salt was prepared from the well-crystallised ammonium salt which is formed by the action of ammonium carbonate on barium iodate even at ordinary temperatures.

2nd Sup.

I on $\text{ClO}^2$	.	.	no action in the dry state, and very little in presence of water.
Br on $\text{HClO}^2$	.	.	production of $\text{HBrO}^2$ , but in very small quantity.
Br on $\text{HClO}^4$	.	.	production of $\text{HBrO}^4$ , but only under peculiar conditions, not easy to determine.
I on $\text{HClO}^4$	.	.	$\text{HClO}^4 + \text{I} = \text{Cl} + \text{HIO}^4$ , the reaction complete on heating.
Cl on $\text{HBrO}^2$	.	.	no action.
I on $\text{HBrO}^2$	.	.	$\text{HBrO}^2 + \text{I} = \text{Br} + \text{HIO}^2$ .
Cl on $\text{HIO}^2$	.	.	no action.
Cl on $\text{HIO}^4$	.	.	no action.
Br on $\text{HIO}^4$	.	.	no action.

**HAMARTITE.** The mineral from the Bastnäs mine, near Riddarhyttan in Sweden, called *Hydrofluocerite*, and represented, according to Hisinger's analysis (1838), by the formula  $\text{Ce}^2\text{F}^2\text{O}^2 + 4\text{H}^2\text{O}$  (i. 834), appears, from an analysis by A. E. Nördenskjöld (*Pogg. Ann.* cxxvi. 628), to be a mixture of a carbonate with a fluoride having the composition  $2(\text{LaO} ; \text{CeO})\text{CO}^2 + \text{CeF}^2$ .

	LaO	CeO	$\text{CO}^2$	$\text{H}^2\text{O}$	F and O (Loss)
Found . . .	45.77	28.49	19.50	1.00	5.23
Calculated . . .	46.15	28.60	20.20	—	5.05

Nördenskjöld proposes to replace the old name, now become inapplicable, by the name *Hamartite*. The mineral occurs, between crystals of allanite, in small wax-yellow druses having a fatty lustre; it exhibits cleavage-planes, probably parallel to the faces of a rhombic prism, and two pairs of faces. Sp. gr. = 4.93; hardness = 4. Before the blowpipe it blackens and gives off a very small quantity of water, then becomes whitish-yellow, fissured, and opaque, but does not melt. Fused with potassium sulphate, it gives a distinct fluorine reaction. After ignition it dissolves easily in sulphuric acid with evolution of hydrofluoric acid.

**HARTITE.** This fossil resin, from the lignite of Oberdorf, near Voitsberg in Styria, occurs sometimes in small fragments or as a coating, sometimes in crystals having a magnitude of 6 to 8 and 4 to 6 mm. The crystals are triclinic, having the axial angles,  $cb = 74^\circ$ ,  $ca = 86^\circ$ , and  $ab = 80^\circ 15'$ , where  $a < b < c$ . The observed faces, in the order of their predominance, are:  $\infty P^\infty$ .  $\infty P^\infty$ .  $oP$ .  $P$ .  $\infty P$ .  $\infty P^u$ . The prisms sometimes exhibit homimorphism. The pinacoids are often curved, even to the shape of hooks. Cleavage parallel to the pinacoids. Sp. gr. = 1.051. It melts at  $74^\circ$ , and at  $150^\circ$  gives off bubbles of vapour, the temperature, however, not becoming stationary even at  $340^\circ$ ; it solidifies from fusion at  $65^\circ$ , becomes negatively electric by friction. Its composition, according to analyses by F. Ullik, and that of Schrötter already given (iii. 14), agrees with the formula  $\text{C}^8\text{H}^{10}$ , which requires 87.8 p.c. carbon and 12.2 hydrogen (*J. Rumpf, J. pr. Chem.* cvii. 189).

**HAUYNE.** Kennigott (*ibid.* cvi. 65) has endeavoured to bring the different analyses of this mineral into accordance without the assumption of isomorphous replacement between  $\text{Na}^2\text{O}$  and  $\text{CaO}$ . In explanation of the differences between the analyses, he adduces the fact that water extracts from pulverised hauyne a substance which remains in small crystals as the water evaporates, and appears, from his observations, to be sodium sulphate. Presuming that a similar process takes place in nature, he supposes that all the analyses of the mineral have been made with substance which had previously lost soda and sulphuric acid. He therefore makes up the amount of  $\text{Na}^2\text{O}$  to 1 molecule for every  $2\text{SiO}^2$ , and adds to the quantity of  $\text{SO}^2$ , found by analysis, a quantity equivalent to this additional quantity of  $\text{Na}^2\text{O}$ . According to this method of recalculation, the four most exact analyses of hauyne give very nearly the proportion:



leading to the formula  $3(\text{Na}^2\text{O}.\text{SiO}^2 + \text{Al}^2\text{O}^3.\text{SiO}^2) + 2(\text{CaO}.\text{SO}^2)$ .

**HAUYNOPHYTE.** The microscopic structure of this lava from the Valtaro near Meli has been examined by F. Zirkel (*Jahrbuch für Mineralogie*, 1870, 818). The hauynes, whose actual substance is either colourless or blue, are essentially altered in colour by numerous gas-pores and imbedded pieces of glassy substance, also by lamellae of ferric oxide. The rock also contains leucite rich in enclosed liquids; nephelin without foreign enclosures; augite, melilite, magnetic iron ore, and apatite. Olivine and feldspar are absent.

**HAY.** See FODDER.

**HEAT.** *Calorimetry.*—Bunsen (*Pogg. Ann.* cxli. 1; *Phil. Mag.* [4], xli. 61; *Chem. Soc. J.* [2], ix. 180) has devised a new method of calorimetry, which is appli-

cable to small quantities of material, and thus facilitates the estimation of the specific heat of rare substances.

It depends on the principle of measuring the quantity of ice melted by a heated body by the diminution of volume which the ice undergoes in melting.

The instrument consists of a glass vessel *a* (fig. 16) in the form of a test-tube, fused into a vessel *b*, which terminates in the bent tube *c*. Into the upper extremity of this tube a graduated tube *s* of small calibre is inserted, and luted with fine sealing-wax into a cork *k*. An iron collar *d* serves the double purpose of containing mercury to render the joint perfect, and affording the means of clamping the instrument to a firm support.

The inner vessel *a* is filled with boiled water from  $\mu$  to  $\alpha$ , as also is the outer vessel from  $\beta$  to  $\lambda$ . The rest of the apparatus from  $\beta$  to  $\gamma$  is filled with boiled mercury.

A cylinder of ice is formed in the vessel *b* by surrounding the whole instrument with snow. When the water congeals, the mercury is driven out through the tube *c*. The scale-tube *s* is inserted into its place, and the mercury thread adjusted to the desired position either by depressing the cork, or in a manner which will be described further on. The substance to be examined, after it has been heated sufficiently and its temperature noted, is allowed to drop into the water in the tube *a*. In the bottom of this tube a piece of cotton-wool is placed and kept in position by means of a piece of platinum wire coiled round it. This prevents breakage, and facilitates the extraction of the substance after the operation is completed. The tube *a* is closed with a cork, to prevent change of air.

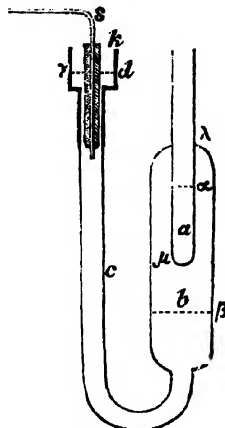


FIG. 16.

When the heated body under examination is introduced into the vessel *a*, some of the surrounding ice is melted, and the volume becomes less. The mercury below rises, and indicates its rise by the retraction in the graduated tube *s*. For relative measurements of the amount of heat given up by substances, it is sufficient to observe the number of divisions through which the mercury is drawn back. To convert these readings into thermal units they must be multiplied by a constant to be determined for each instrument by a method described in Bunsen's paper.

As the cylinder of ice surrounding the inner vessel weighs from 40 to 50 grams, and the quantity of ice melted in a single determination of specific heat does not exceed about 0.35 gram, it is easily seen that one cylinder of ice will suffice for about 100 such determinations, so that the apparatus once set up in the manner above described, may be used for weeks if the snow surrounding it be renewed every morning and evening. The accuracy of the determinations depends in great part on the care with which the water and mercury in the instruments have been freed from absorbed air. The delicacy of the instrument is shown by the fact that the rise of temperature, produced by immersing in the water 0.4 gram of brass at 37°, which would amount to only 0.07° of the centigrade thermometer, will move the quicksilver thread of the calorimeter through 20 divisions of the scale, each measuring a millimeter.

**Specific Heat.** For Bunsen's determinations of the specific heats of elementary bodies by the method above described, see *First Supplement*, p. 665.

**Specific Heat of Carbon.**—The numbers found by different observers for the specific heat of the allotropic modifications of carbon agree, as the following table shows, so little with each other, that their difference cannot be explained by the different methods of observation, or by the impurities of the substances employed:—

Observer	Charcoal	Gas Carbon	Natural Graphite	Blast Furnace Graphite	Diamond	Interval of temperature
Rognault	0.2415	0.2036	0.2010	0.1970	0.1469	8°—08°
De la Rive and Marcet	0.2009	—	—	—	0.1146	3°—14°
Kopp	—	0.185	0.174	0.165	—	22°—52°
Wüllner and Bettendorf	—	—	0.1919	—	0.1452	22°—70°

These differences may, however, be accounted for by the rapid increase of the specific heat of carbon with the temperature. II. F. Weber (*Deut. Chem. Ges. Ber.* v. 303) finds indeed that the specific heat of this element increases with the temperature far more rapidly than that of any other substance; the specific heat of the diamond, for example, becoming three times as great when the temperature rises from 0° to 200°.

Weber has determined the specific heat of the diamond for twelve different temperatures at about equal intervals between 0° and 200°, and finds that the mean specific heat  $C_{0-t}$ , between 0° and the temperature  $t$ , may be calculated by the formula—

$$C_{0-t} = 0.0947 + 0.000497t - 0.00000012t^2 \quad \dots \quad (1)$$

This rapid variation with the temperatures, however, renders the *mean* specific heat of but little value, and it becomes necessary to calculate from it the *true* specific heat for the temperature  $t$ , that is to say, the quantity of heat required to increase the unit of weight of the substance at  $t^\circ$  by 1 degree. This true specific heat  $\gamma_t$  may be calculated from the formula—

$$t.C_{0-t} = \int_0^t \gamma_t dt \quad \dots \quad (2)$$

whence by differentiation—

$$\gamma_t = 0.0947 + 0.000994t - 0.00000036t^2 \quad \dots \quad (3)$$

This formula gives the following values for the specific heats at intervals of 50° between 0° and 200°—

Temperatures	0°	50°	100°	150°	200°
Actual specific heats	0.0947	0.1435	0.1905	0.2357	0.2791

The specific heat of graphite was found to be 0.1439, between 0° and 34°, and = 0.1967 between 0° and 100°, whenever its mean specific heat between 0° and any temperature  $t$  can be calculated from the formula—

$$C_{0-t} = 0.1167 + 0.0008t,$$

and its true specific heat at any definite temperature  $t$  from—

$$\gamma_t = 0.1167 + 0.0016t.$$

Finally, the specific heat of charcoal was found by De la Rive and Marcet to be 0.2009 between 3° and 14°, and by Regnault = 0.2415 between 8° and 18°, whence it appears that the porous varieties of carbon exhibit variations in their specific heat similar to those observed in graphite and diamond.

The great increase in the specific heat of carbon as its temperature rises is quite sufficient to account for its deviation from the law of Dulong and Petit. If, however, the equation (3) be supposed to hold good for diamond up to the temperature of 500° (which is probably not strictly true), the specific heat of diamond at about 525° would be 0.52, which would be quite in accordance with the law in question, since  $0.52 \times 12 = 6.24$ .

The specific heat of carbon at temperatures considerably above those above mentioned has been determined by Dewar (*Phil. Mag.* [4], xlv. 461). To determine the mean specific heat between 20° and 1040°, gas-carbon, graphite, cocoa-nut charcoal and diamond were heated in an iron tube in boiling zinc (temp. about 1040°) and then plunged into a water-calorimeter. The mean value of the specific heat deduced from the results was 0.32.

To determine it at much higher temperatures, a cubical block of lime 2 inches in the side was pierced to the centre with two channels a quarter of an inch wide, and in directions at right angles to each other. Generally only one of the channels passed entirely through the mass. Two powerful oxy-hydrogen flames were caused to play into these holes till the interior was at a white heat. The carbon was then placed at the point of meeting of the holes, and kept exposed to the oxy-hydrogen flame for a considerable time, whereby it was exposed to a heat estimated at 2100°, after which it was allowed to drop from the mass of lime into the calorimeter.

The mean specific heat deduced from these experiments was 0.42, and Dewar is of opinion that the true specific heat at about 2000° must be at least 0.5. If it be so, carbon conforms at these high temperatures also to the law of Dulong and Petit.

*Specific Heat of Solutions.*—J. Thomsen (*Pogg. Ann.* cxlii. 337) has determined the specific heats of the aqueous solutions of several acids, alkalis, and salts by observing the rise of temperature produced in about 1000 cub. cent. of the solution contained in a calorimeter by the combustion of a given volume of hydrogen, and comparing the result with the rise produced under like conditions in a known weight of water.

The results are given in the following table, in which column 1 gives the number of molecules of water ( $n$ ) present in the solution for one molecule of the substance dissolved; column 2 the specific heat of this solution; column 3 its molecular weight, or

more strictly, the weight corresponding with the chemical formula of the solution. It is given in two terms, the first being the molecular weight of the substance in solution, the second the sum of the weights of the molecules of water. Column 4 gives the molecular heat of the solution, i.e. the products of its specific heat and molecular weight; column 5, the difference between this molecular heat and the heat which would be required by the water of the solution alone; column 6 gives the specific gravity of the solutions; column 7, their molecular volume; and lastly, column 8, the difference between this volume and that of the water alone.

*Specific Heat of Solutions.*

1	2	3	4	5	6	7	8
n	Specific Heat	Molecule	Molecular Heat	Difference	Specific Gravity	Molecular Volume	Difference
<i>Sulphuric Acid, SO<sup>3</sup> + nH<sup>2</sup>O.</i>							
5	0.545	80 + 90	92.7	+ 2.7	1.4723	115.5	+ 25.5
10	0.700	80 + 180	182.0	+ 2.0	1.2870	202.0	+ 22.0
20	0.821	80 + 360	361.2	+ 1.2	1.1593	379.6	+ 19.6
50	0.918	80 + 900	900	0	1.0692	916.6	+ 16.6
100	0.956	80 + 1800	1797	- 3	1.0355	1815.5	+ 15.5
200	0.977	80 + 3600	3595	- 5	1.0180	3615.4	+ 15.4
<i>Nitric Acid, NO<sup>3</sup>H + nH<sup>2</sup>O.</i>							
10	0.768	63 + 180	186.6	+ 6.6	1.1512	210.5	+ 30.5
20	0.819	63 + 360	359.1	- 0.9	1.0851	389.8	+ 20.8
50	0.930	63 + 900	896	- 4	1.0360	929.5	+ 29.5
100	0.963	63 + 1800	1794	- 6	1.0185	1829.2	+ 20.2
200	0.982	63 + 3600	3597	- 3	1.0094	3629.0	+ 20.0
<i>Hydrochloric Acid, HCl + nH<sup>2</sup>O.</i>							
10	0.719	36.5 + 180	162.2	- 17.8	1.0832	199.0	+ 10.0
20	0.855	36.5 + 360	338.9	- 21.0	1.0456	379.2	+ 19.2
50	0.932	36.5 + 900	873	- 27	1.0193	918.8	+ 18.8
100	0.964	36.5 + 1800	1770	- 30	1.0100	1818.5	+ 18.5
200	0.979	36.5 + 3600	3561	- 39	1.0052	3617.7	+ 17.7
<i>Tartaric Acid, C<sup>4</sup>H<sup>6</sup>O<sup>6</sup> + nH<sup>2</sup>O.</i>							
10	0.745	150 + 180	246	+ 66	1.2409	265.9	+ 85.9
25	0.856	150 + 450	513	+ 63	1.1229	534.3	+ 84.3
50	0.911	150 + 900	957	+ 57	1.0677	983.4	+ 83.4
100	0.952	150 + 1800	1856	+ 56	1.0358	1882.5	+ 82.5
200	0.975	150 + 3600	3656	+ 66	1.0186	3681.3	+ 81.3
<i>Sodium Hydrate, NaOH + nH<sup>2</sup>O.</i>							
7½	0.847	40 + 135	148.2	+ 13.2	1.2576	130.2	+ 4.2
15	0.878	40 + 270	272.2	+ 2.2	1.1450	270.7	+ 0.7
30	0.919	40 + 540	533	- 7	1.0782	537.0	- 2.1
50	0.942	40 + 900	885	- 15	1.0486	806.4	- 3.6
100	0.968	40 + 1800	1781	- 19	1.0246	1795.9	- 4.1
200	0.983	40 + 3600	3578	- 22	1.0124	3594.8	- 5.2

*Specific Heat of Solutions.*

1	2	3	4	5	6	7	8
n	Specific Heat	Molecule	Molecular Heat	Difference	Specific Gravity	Molecular Volume	Difference
<i>Potassium Hydrate, KHO + nH<sup>2</sup>O.</i>							
30	0.876	56 + 540	522	- 18	1.0887	547.5	+ 7.5
50	0.916	56 + 900	876	- 21	1.0550	906.3	+ 6.3
100	0.954	56 + 1800	1770	- 30	1.0284	1804.9	+ 4.9
200	0.975	56 + 3600	3565	- 35	1.0144	3604.1	+ 4.1
<i>Ammonium Hydrate, NH<sup>4</sup>.OH + nH<sup>2</sup>O.</i>							
30	0.907	35 + 540	573	+ 33	0.9878	582.1	+ 42.1
50	0.909	35 + 900	934	+ 34	0.9927	941.0	+ 41.0
100	0.999	35 + 1800	1833	+ 33	0.9907	1841.2	+ 41.2
<i>Sodium Chloride, NaCl + nH<sup>2</sup>O.</i>							
10	0.791	58.5 + 180	188.5	+ 8.5	1.1872	200.0	+ 20.0
20	0.863	58.5 + 360	361.0	+ 1.0	1.1033	379.3	+ 19.3
30	0.895	58.5 + 540	536	- 4	1.0718	558.4	+ 18.4
50	0.931	58.5 + 900	892	- 8	1.0444	917.8	+ 17.8
100	0.962	58.5 + 1800	1788	- 12	1.0234	1816.1	+ 16.1
200	0.978	58.5 + 3600	3578	- 22	1.0118	3616.0	+ 16.0
<i>Potassium Chloride, KCl + nH<sup>2</sup>O.</i>							
15	0.761	74.6 + 270	262.4	- 7.6	1.1468	300.4	+ 30.4
30	0.850	74.6 + 540	522.4	- 17.4	1.0800	569.0	+ 29.0
50	0.904	74.6 + 900	881	- 10	1.0496	928.2	+ 28.2
100	0.948	74.6 + 1800	1775	- 25	1.0258	1827.3	+ 27.3
200	0.970	74.6 + 3600	3565	- 35	1.0136	3625.0	+ 25.0
<i>Ammonium Chloride, NH<sup>4</sup>Cl + nH<sup>2</sup>O.</i>							
7½	0.760	53.5 + 135	143.3	+ 8.3	1.0718	175.9	+ 40.9
10	0.778	53.5 + 180	181.6	+ 1.6	1.0664	210.0	+ 39.0
25	0.881	53.5 + 450	443.6	- 6.4	1.0314	488.2	+ 38.2
50	0.937	53.5 + 900	893	- 7	1.0167	937.8	+ 37.8
100	0.966	53.5 + 1800	1791	- 9	1.0086	1837.7	+ 37.7
200	0.982	53.5 + 3600	3588	- 12	1.0044	3637.6	+ 37.6
<i>Sodium Nitrate, NaNO<sup>3</sup> + nH<sup>2</sup>O.</i>							
10	0.769	85 + 180	203.8	+ 23.8	1.2474	212.5	+ 32.5
25	0.863	85 + 450	481.7	+ 11.7	1.1187	480.4	+ 30.4
50	0.918	85 + 900	904	+ 4	1.0800	929.2	+ 29.2
100	0.950	85 + 1800	1791	- 0	1.0311	1828.2	+ 28.2
200	0.975	85 + 3600	3594	- 7	1.0160	3627.0	+ 27.0

*Specific Heat of Solutions.*

1	2	3	4	5	6	7	8
"	Specific Heat	Molecule	Molecular Heat	Difference	Specific Gravity	Molecular Volume	Difference
<i>Potassium Nitrate, <math>\text{KNO}_3 + n\text{H}_2\text{O}</math>.</i>							
25	0.832	101 + 450	458.4	+ 8.4	1.1228	490.7	+ 40.7
50	0.901	101 + 900	902	+ 2	1.0651	939.8	+ 39.8
100	0.942	101 + 1800	1791	- 9	1.0336	1839.2	+ 39.2
200	0.966	101 + 3600	3575	- 25	1.0173	3638.3	+ 38.3
<i>Ammonium Nitrate, <math>\text{NH}_4\text{NO}_3 + n\text{H}_2\text{O}</math>.</i>							
5	0.697	80 + 90	118.7	+ 28.7	1.2046	141.1	+ 51.1
20	0.859	80 + 360	378.0	+ 18	1.0743	409.8	+ 49.6
50	0.929	80 + 900	910	+ 10	1.0331	948.6	+ 48.6
100	0.962	80 + 1800	1808	+ 8	1.0180	1846.8	+ 46.8
<i>Sodium Carbonate, <math>\text{Na}_2\text{CO}_3 + n\text{H}_2\text{O}</math>.</i>							
50	0.896	106 + 900	901	+ 1	1.1131	903.8	+ 3.8
100	0.933	106 + 1800	1778	- 22	1.0593	1799.3	- 0.7
200	0.958	106 + 3600	3550	- 50	1.0306	3596.0	- 4.0
<i>Sodium Sulphate, <math>\text{Na}_2\text{SO}_4 + n\text{H}_2\text{O}</math>.</i>							
65	0.892	142 + 1170	1170	0	1.1010	1191.6	+ 21.6
100	0.920	142 + 1800	1787	- 13	1.0675	1819.5	+ 19.2
200	0.955	142 + 3600	3574	- 26	1.0350	3615.4	+ 15.4
<i>Ammonium Sulphate, <math>(\text{NH}_4)_2\text{SO}_4 + n\text{H}_2\text{O}</math>.</i>							
30	0.820	132 + 540	551	+ 11	1.1148	602.8	+ 62.8
50	0.871	132 + 900	899	- 1	1.0774	267.6	+ 67.6
100	0.924	132 + 1800	1785	- 15	1.0420	1854.1	+ 54.1
200	0.959	132 + 3600	3579	- 21	1.0214	3653.8	+ 53.8
<i>Magnesium Sulphate, <math>\text{MgSO}_4 + n\text{H}_2\text{O}</math>.</i>							
20	0.744	120 + 360	357	- 3	1.2864	373.1	+ 13.1
50	0.867	120 + 900	874	- 26	1.1253	906.4	+ 6.4
100	0.917	120 + 1800	1761	- 39	1.0649	1803.0	+ 3.0
200	0.952	120 + 3600	3541	- 59	1.0334	3599.8	- 0.2
<i>Sodium Acetate, <math>\text{NaC}_2\text{H}_3\text{O}_2 + n\text{H}_2\text{O}</math>.</i>							
20	0.884	82 + 360	391	+ 31	1.0993	402.1	+ 42.1
50	0.938	82 + 900	921	+ 21	1.0442	940.4	+ 40.4
100	0.965	82 + 1800	1817	+ 17	1.0230	1839.7	+ 39.7
200	0.983	82 + 3600	3620	+ 20	1.0120	3638.3	+ 38.3

*Specific Heat of Solutions.*

n + 200H <sup>2</sup> O.								
1	2	3	4	5	6	7	8	
KBr	0.962	119 + 3600	3578	- 22	1.0236	3633	+ 33	
NH <sup>4</sup> Br	0.968	98 + 3600	3580	- 20	1.0154	3642	+ 42	
NaI	0.954	150 + 3600	3578	- 22	1.0318	3634	+ 34	
KI	0.950	166 + 3600	3578	- 22	1.0355	3644	+ 44	
NH <sup>4</sup> I	0.963	145 + 3600	3606	+ 6	1.0248	3654	+ 54	
BaCl <sup>2</sup>	0.932	208 + 3600	3549	- 51	1.0502	3626	+ 26	
CaCl <sup>2</sup>	0.957	111 + 3600	3551	- 49	1.0253	3619	+ 19	
K <sup>2</sup> O.SO <sup>3</sup>	0.940	174 + 3600	3548	- 52	1.0380	3636	+ 36	
ZnO.SO <sup>3</sup>	0.947	161 + 3600	3562	- 38	1.0455	3598	- 2	
FeO.SO <sup>3</sup>	0.951	152 + 3600	3568	- 32	1.0413	3603	+ 3	
CuO.SO <sup>3</sup>	0.953	159 + 3600	3583	- 17	1.0444	3599	- 1	
BaO.N <sup>2</sup> O <sup>3</sup>	0.933	261 + 3600	3602	+ 2	1.0584	3648	+ 48	
PbO.N <sup>2</sup> O <sup>3</sup>	0.919	331 + 3600	3613	+ 13	1.0771	3649	+ 49	

The numbers in column 4 of the preceding tables express the *water-value* of the solution, that is the weight of water which requires the same amount of heat as the molecular weight of the solution, and the table shows that this water-value differs in most cases but little from the amount of water present in the solution. In the case of sulphuric acid for example, the solution with 5 molecules of water has a water-value of 92.7, the weight of the molecules of water in the solution being 90, that of the whole molecule 170; in the solution with 50 molecules of water, these values are 900, 900 and 980 respectively. In still more dilute solutions the water-value sinks even below the molecular weight of the water actually present. Similar phenomena are observed in most other solutions. The differences in column 5 are generally positive in concentrated solutions, gradually sink to zero, and become negative in dilute solution. In some few cases, as with hydrochloric acid and potassium hydrate, they are always negative.

Previous researches by other experimenters, as well as those of Thomsen, have shown that when an aqueous solution is mixed with water, contraction takes place, i.e. the volume of the solution is less than the sum of the volumes of the constituent liquids; thus (p. 597) 270.7 volumes of a soda-solution NaHO + 15H<sup>2</sup>O, mixed with 15 molecules or 270 volumes of water, give, not 540, but only 537.9 volumes; and the foregoing experiments show that when an aqueous solution is mixed with water, the resulting solution has a lower molecular heat than the sum of the molecular heats of the constituents; e.g. the same soda-solution requires 272.2 units of heat to raise its temperature by a certain amount; but when mixed with 270 grams of water it requires for that purpose, not 542.2, but only 533 units. A similar relation is found when acids and alkalis are mixed. When potash or soda is neutralised with hydrochloric, nitric, or sulphuric acid, the molecular heat of the resulting compound is higher than the sum of the molecular heats of the constituents, while on the other hand it is found that these potassium and sodium salts have a molecular volume greater than the sum of the volumes of their constituents; in other words expansion has taken place during combination. In the case of ammonia salts the reverse takes place. Contraction is the result of the combination, and the molecular heat of the compound is less than the sum of the molecular heats of the constituents.

Marignac (*N. Arch. Ph. Nat.* xxxix. 217) has estimated the specific heats of various aqueous solutions, and of the solution of sulphur, phosphorus, iodine, and bromine in carbon sulphide, by determining the relative weights of water and of the liquid under examination, which are heated to the same temperature by equal quantities of heat. The source of heat was a mercurial thermometer with a large bulb, heated to 65-10°. Marignac's results with sulphuric acid, hydrochloric acid, and sodium chloride, agree nearly with those of Thomsen. The following table contains his determinations of the specific heats of other aqueous solutions of the two sodium sulphates and of sugar, and those of the solutions of the bodies above mentioned in carbon sulphide. The numbers in the several columns have the same signification as those in the first four columns of Thomsen's table.



*Specific Heats of Aqueous Solutions.*

n	Specific Heat	Molecular Weight	Molecular Heat
<i>Sodium Sulphate, Na<sup>2</sup>SO<sup>4</sup> + nAq.</i>			
50	0.8890	1042	926.3
100	0.9345	1942	1815
200	0.9625	3742	3602
400	0.9805	7312	7199
<i>Sodium-Hydrogen Sulphate, NaHSO<sup>4</sup> + nAq.</i>			
25	0.8683	570	495
50	0.9146	1020	933
100	0.9497	1920	1823
200	0.9719	3720	3615
<i>Sugar, C<sup>12</sup>H<sup>22</sup>O<sup>11</sup> + nAq.</i>			
25	0.7558	792	598.6
50	0.8425	1242	1046
100	0.9091	2442	1947
200	0.9500	3942	3745
400	0.9742	7542	7347

*Specific Heats of Solutions in Carbon Sulphide.*

n	Specific Heat	Molecular Weight	Molecular Heat
<i>Sulphur, S + nCS<sup>2</sup>.</i>			
1	0.229	108	24.7
2	0.232	184	42.8
4	0.232	336	77.9
10	0.235	792	186.0
<i>Phosphorus, P + nCS<sup>2</sup>.</i>			
1	0.219	50	10.9
1	0.222	69	15.3
1	0.225	107	24.2
2	0.229	183	41.9
4	0.2295	335	76.9
<i>Iodine, I + nCS<sup>2</sup>.</i>			
10	0.219	887	194
20	0.228	1647	376
<i>Bromine, Br + nCS<sup>2</sup>.</i>			
1	0.174	156	27.1

These solutions in carbon-sulphide differ considerably in their behaviour from aqueous solutions of acids and salts. The molecular heat of the mixture of bromine and carbon sulphide is exactly equal to the sum of the molecular heats of the two liquids. In like manner iodine dissolves in carbon sulphide without perceptible diminution of the specific heat which belongs to it in the fused state. When diminution takes place, as in the case of sulphur and phosphorus, it is confined within narrow limits, and the molecular heat of the solution never becomes less than that of the solvent alone.

Respecting the Specific Heats of Mixtures of Ethyl Alcohol and Methyl Alcohol with Water, see *ETHYL ALCOHOL* (p. 475) and *METHYL ALCOHOL*; of Ethyl Alcohol with Carbon Sulphide, Chloroform, and Benzene, see p. 477.

*Relations between the Specific Heats of Mixtures and the Heat evolved in their Formation.*—These relations have been investigated by A. Dupré (*Proc. Roy. Soc.* xx, 336), chiefly in the case of mixtures of methyl alcohol and water.

1. The difference between the number of heat-units evolved during the mixing of given weights of two substances, at the temperatures  $t$  and  $t'$  respectively, is equal to the difference between the number of heat-units required to raise the mixture, and that required to raise the two constituents taken separately, from the lower to the higher temperature. Or let  $U$  and  $U'$  be the units of heat evolved by mixing  $x$  and  $y$  at the temperatures  $t$  and  $t'$  respectively;  $S$ ,  $S'$ , and  $S''$ , the specific heat of the mixture  $z$  and its constituents  $x$  and  $y$  respectively; then

$$U - U' = z \cdot S(t - t') - \{x \cdot S'(t - t') + yS''(t - t')\}.$$

2. If more units of heat are evolved at the higher than at the lower temperature, the specific heat of the resulting mixture will be below the calculated mean, and *vice versa*.

3. The absorption of a lesser number of heat-units will of course be equivalent to the evolution of a greater number, while the absorption of a greater number will be equivalent to the evolution of a smaller number of heat-units.

A great many mixtures of various liquids have been found to conform as closely as can be expected with proposition 1. If these propositions prove to be an exposition of a general law, it will be possible to calculate the specific heat of one constituent of a mixture or solution, if the specific heat of the other constituent, the specific heat of the mixture, and the heat evolved or absorbed at two different temperatures between which these specific heats have been estimated, be known. It will also be possible to compare the specific heats of liquid and solid substances when both are placed under similar conditions.

**Expansion by Heat.** 1. *Of Gases.* Amagat (*N. Arch. Phys. Nat.* xl, 320; xli, 365) has determined the expansions of sulphurous anhydride and carbonic anhydride, as compared with air between the temperatures of  $0^\circ$  and  $250^\circ$ . The following table gives the numbers calculated from the experimental data, the expansion-coefficient of air between the above limits being supposed to be constant and equal to 0.00367:—

	Sulphurous Anhydride	Carbonic Anhydride
At $0^\circ$ . . . . .	—	0.003724
Between $0^\circ$ and $10^\circ$ . . . . .	0.004233	—
" $10^\circ$ and $20^\circ$ . . . . .	0.004005	—
At $50^\circ$ . . . . .	0.003846	0.003704
" $100^\circ$ . . . . .	0.003757	0.003695
" $150^\circ$ . . . . .	0.003718	0.003690
" $200^\circ$ . . . . .	0.003695	0.003687
" $250^\circ$ . . . . .	0.003685	0.003682

The coefficient of expansion of sulphurous anhydride decreases with increasing temperature, at first rapidly, up to a temperature of  $50^\circ$ , and then slowly up to about  $250^\circ$ , above which it apparently remains constant. It appears, therefore, to tend towards a limit different from that of atmospheric air, namely 0.00374. Carbonic anhydride shows a similar result; the coefficient diminishes, though slightly, up to about  $200^\circ$ , above which temperature it appears to remain constant at 0.003696, or also slightly higher than that of atmospheric air.

2. *Of Aqueous Solutions.*—Marignac (*Ann. Chem. Phys.* [4], xxii, 415) has made a series of observations on the density and expansibility of aqueous solutions.

the expansion being measured by means of dilatometers—that is, large-sized thermometers with bulbs of 25 to 28 c.c. capacity. The divisions on the stem allowed variations amounting to no more than  $\frac{1}{10000}$  of the total volume to be read off. No perceptible variation could be detected in the volume of a solution, when kept at a constant temperature during several days, the first observation being made as soon as possible after the solution was prepared.

The following tables give the densities, molecular volumes, and coefficient of expansion, at 20°, of various aqueous solutions. Column *n* gives the number of molecules of water present; D, the density of the solution; W, its molecular weight; V, its molecular volume (water = 18);  $V - 18n$ , the difference between the molecular volume of the solution and that of the water which it contains; E, the coefficient of expansion; all at 20°.

*Sulphuric Acid, H<sup>2</sup>SO<sup>4</sup> + nAq.*

<i>n</i>	D	W	V	$V - 18n$	E
0	1.83211	98	53.40	53.40	0.0005585
5	1.41317	188	132.80	42.80	0.0005660
10	1.26099	278	220.08	40.08	0.0005845
15	1.19033	368	308.60	38.60	0.0005697
25	1.12202	548	487.14	37.14	0.0004975
50	1.06451	998	935.9	35.9	0.0003867
100	1.03251	1898	1835.0	35.0	0.0003107
200	1.01502	3698	3633.6	33.6	0.0002602
400	1.00728	7298	7232.8	32.8	0.0002339
Water	0.99826	18	18	—	—

The continued decrease of the numbers in the last column shows that, whether sulphuric acid itself be mixed with water, or a dilute sulphuric acid be still further diluted, contraction always results.

*Sodium Sulphate, Na<sup>2</sup>SO<sup>4</sup> + nAq.*

<i>n</i>	D	W	V	$V - 18n$	E
25	1.23443	592	478.7	28.7	0.0004102
50	1.12645	1042	923.4	23.4	0.0003608
100	1.06546	1942	1819.5	19.5	0.0003051
200	1.03287	3742	3616.6	16.6	0.0002599
400	1.01586	7342	7214.8	14.8	0.0002344

This table shows that contraction takes place when a solution of sodium sulphate is diluted with water.

*Acid Sodium Sulphate, NaHSO<sup>4</sup> + nAq.*

<i>n</i>	D	W	V	$V - 18n$	E
25	1.17053	570	486.1	36.1	0.0005554
50	1.09168	1020	932.7	32.7	0.0004349
100	1.04718	1920	1830.3	30.3	0.0003390
200	1.02367	3720	3628.0	28.0	0.0002776

*Comparative Table of the Molecular Volumes of Solutions of Neutral Sodium Sulphate, Acid Sodium Sulphate, and Sulphuric Acid.*

<i>n</i>	H <sup>2</sup> SO <sup>4</sup>	NaHSO <sup>4</sup>	Na <sup>2</sup> SO <sup>4</sup>
25	487.1	486.1	478.7
50	935.9	932.7	923.4
100	1835.0	1830.3	1819.5
200	3633.6	3628.0	3616.6
400	7232.8	—	7214.8

It will be seen that the molecular volume of the acid sulphate is always above that of the mean of the sulphuric acid and neutral sulphate; so that when a solution of neutral sulphate is mixed with sulphuric acid, expansion *always* takes place.

*Hydrochloric Acid, HCl + nAq.*

n	D	W	V	V-18n	E
6.25 . . .	1.12030	149	132.77	20.27	0.0004546
12.50 . . .	1.06700	261.5	244.65	19.65	0.0003460
25 . . . .	1.03500	486.5	460.23	19.23	0.0002799
50 . . . .	1.01755	936.5	918.75	18.75	0.0002394
100 . . . .	1.00815	1836.5	1818.42	18.42	0.0002240
200 . . . .	1.00330	3636.5	3618.23	18.23	0.0002107

*Sodium Chloride, NaCl + nAq.*

n	D	W	V	V-18n	E
12.5 . . .	1.15292	283.5	245.47	20.47	0.0004135
25 . . . .	1.08207	508.5	469.12	19.12	0.0003530
60 . . . .	1.04227	958.5	918.02	18.02	0.0002960
100 . . . .	1.02069	1858.5	1817.06	17.66	0.0002532
200 . . . .	1.00965	3658.5	3617.58	17.58	0.0002305.

*Sugar, C<sup>12</sup>H<sup>22</sup>O<sup>11</sup> + nAq.*

n	D	W	V	V-18n	E
25 . . . .	1.19242	792	663.0	213.0	0.0003434
50 . . . .	1.11506	1242	1111.9	211.0	0.0002985
100 . . . .	1.06333	2142	2010.0	210.9	0.0002595
200 . . . .	1.03265	3942	3810.8	210.8	0.0002312
400 . . . .	1.01594	7542	7410.8	210.8	0.0002118

These results show that, in a mixture of a solution with water, the coefficient of expansion of the mixture is higher than the mean of the coefficients of expansion of the two constituent liquids. They also confirm the general law that the dilution of a solution is attended with contraction. This contraction, however, diminishes as the temperature at which the mixture is made rises, so that it seems very probable that at temperatures sufficiently elevated the dilution of a solution would no longer be accompanied by contraction of volume.

As a general result of his experiments on the specific heat, density, and expansion of solutions, Marignac concludes that the state of combination of a salt in solution is invariable, and is established immediately and finally at the moment of mixture or dilution. This conclusion is strengthened by the fact already noticed that the volume of a solution remains constant at the same temperature, and that the equilibrium of temperature is established as quickly on the mixing of two solutions as on that of two masses of water at different temperatures.

**Fusion and Solidification.** *Determination of Melting Points.*—For the exact determination of melting points, E. Kopp (*Deut. Chem. Ges. Ber.* v. 645) recommends the use of a mercury-bath instead of an oil- or water-bath. The substance is placed on the mercury, and covered with a small funnel of thin glass. The melting point and the solidifying point can be observed most readily if the substance is opaque and becomes transparent when fused. Substances which soften before melting are fused and introduced into a little conical capillary tube, which, after cooling, is placed 0.5 to 1.0 centimeter before the surface of the mercury. As soon as the substance becomes soft or begins to melt, it is forced out of the tube and appears above the surface of the mercury.

*Influence of a Change of Density upon Melting Point.*—In accordance with the mechanical theory of heat, which requires that the melting point be raised or lowered

according as the specific gravity is increased or diminished, F. Mohr (*Ann. Ch. Pharm.* clxii. 61-67) has found by experiment that, in the case of garnets, fusion lowers the melting point at the same time that it diminishes the specific gravity.

*Melting and Solidifying Points of Fats.*—F. Rüdorff (*Pogg. Ann.* cxlv. 279), after testing all the usual methods for determining the melting points of fats, finds that the most concordant results are obtained by covering a thermometer-bulb with a layer of fat about 3 mm. thick, immersing it in hot water, and observing the temperatures at which the fat begins to separate from the bulb and to ascend through the water.

The solidifying points of some fats were determined by observing the temperatures at which they became solid whilst they were violently agitated; but with the glycerides and some other fats; which exhibit a rise of temperature during solidification, it was found best to take as solidifying point that temperature to which the thermometer rises during solidifying.

The following table exhibits the results :—

	Melts at	Solidifies at	Temperature rises during solidification to
	°C.	°C.	
Yellow bees'-wax . . .	63·4	61·5 62·6 62·3	— — —
White bees'-wax . . .	61·8	61·6	—
Paraffin . . .	49·6 52·5 to 54 53	49·6 53 52·9	— — —
Spermaceti . . .	52·7 to 53·2 43·5 44·1 to 44·3	52·7 43·4 44·2	— — —
Stearic acid . . .	55·3 56·2 to 56·6 56·0 to 54·4	55·2 55·8 55·7	— — —
Japan wax . . .	50·4 to 51·0	—	50·8
Cacao butter . . .	33·5	—	27·4
Nutmeg butter . . .	70 to 80	—	41·7—41·8
Mutton suet . . .	46·5 to 47·4	32 to 36	Several degrees
Beef suet . . .	43·5 to 45·0	27 to 35	

The phenomenon of a rise of temperature during solidification was also observed in artificial mixtures of fats; for instance, of spermaceti and stearic acid, and of paraffin and stearic acid, and is probably due to the constantly varying composition of the liquid remaining behind during partial solidification. A change in composition as solidification goes on may possibly also explain the great interval of temperature during which beef and mutton suet pass from the liquid into the solid state.

An apparatus for determining the melting points of organic bodies is described by J. Löwe (*Dingl. polyt. J.* cci. 250; *Chem. Soc. J.* [2], ix. 973).

For De Coppet's experiments on the Solidification of Saline Solutions, see *Ann. Chim. Phys.* [4], xxiii. 366; *Chem. Soc. J.* [2], x. 1062.

**Thermic Phenomena accompanying Allotropic and Isomeric Transformation.** According to Berthelot (*Compt. rend.* lxx. 941), 1 gram of octohedral sulphur on dissolving in carbon sulphide absorbs 12,800 units of heat (gram-degrees). According to Person, the heat of fusion of octohedral sulphur is 9,400 units for 1 gram. Berthelot finds, moreover, the transformation of amorphous soluble sulphur into octohedral sulphur under the influence of aqueous sulphydric acid is attended with the absorption of 2,600 units of heat for 1 gram, and that of insoluble sulphur from flowers of sulphur into octohedral sulphur, with the development of 2,700 units. Hence it appears that the transformation of insoluble into octohedral sulphur at 185° is not attended either with evolution or with absorption of heat. The conversion of prismatic into octohedral sulphur develops, according to Mitscherlich, 2,300 units of heat: consequently, the transformation of prismatic into amorphous insoluble sulphur at ordinary temperatures develops about 5,000 units. Accordingly the transformation of dissolved octohedral into insoluble sulphur under the influence of direct sunlight at ordinary temperatures is attended with a development of 12,800 units for 1 gram, and that which takes place in ordinary sulphur at about 113° after fusion is likewise at-

tended with development of heat. Light seems to incite the change, but does not effect the actual work of transformation.

Respecting the heat-phenomena attending the transformation of cyanic acid into cyamelide, and of cyamelide into cyanuric acid, see 1st Suppl. (p. 518).

### Heat of Chemical Action.

#### I. Heat developed in the Combination of the Elementary Bodies.

A. *In the Combinations of Hydrogen with the Non-metallic Elements.*  
—J. Thomsen (*Deut. Chem. Ges. Ber.* iv. 941; v. 789) has determined the affinity of hydrogen for the non-metallic elements, as measured by the quantities of heat evolved in their several combinations, with the following results:—

1. *Chlorine.*—The affinity between hydrogen and chlorine, estimated by burning chlorine in an atmosphere of dry hydrogen, gave—

$$(H, Cl) = 22,000 \text{ heat-units,}$$

a number differing considerably from that obtained by Favre & Silbermann, viz. 23,783 (iii. 100).

For the absorption of hydrochloric acid gas by water, Thomsen finds—

$$(HCl, Aq) = 17,314 \text{ heat-units,}$$

when 400 mol. water are present to each molecule of hydrogen chloride. Hence for the formation of hydrochloric acid in aqueous solution, we have—

$$(H, Cl, Aq) = 39,315 \text{ heat-units.}$$

2. *Bromine.*—The affinity of bromine for hydrogen was determined from the heat evolved in the decomposition of an aqueous solution of potassium bromide by chlorine, which gives—

$$(KBr, Aq, Cl) = 11,478 \text{ heat-units.}$$

Further it is known that  $(Br, Aq) = 539$  h.-u.;  $(H, Cl, Aq) = 39,315$  h.-u.;  $KHO, Aq, HCl, Aq = 13,740$  h.-u. and  $(KHO, Aq, HBr, Aq) = 13,750$  h.-u.: hence, by calculation—

$$(Br, Aq, H) = 27,837 \text{ heat-units,}$$

$$(Br, H, Aq) = 28,376 \text{ „}$$

Further, the absorption of hydrobromic acid gas by water gives

$$(HBr, Aq) = 19,207 \text{ heat-units:}$$

consequently, for the affinity between bromine and hydrogen we have—

$$(H, Br) = 8,440 \text{ heat-units.}$$

3. *Iodine.*—The affinity of hydrogen for iodine was determined in like manner by the decomposition of aqueous potassium iodide with chlorine, which gives—

$$(KI, Aq, Cl) = 26,209 \text{ heat-units,}$$

and the heat of neutralisation of hydriodic acid by potash is  $(KAq, HIAq) = 13,657$  h.-u.; hence the affinity in aqueous hydriodic acid is found to be—

$$(H, I, Aq) = 13,171 \text{ heat-units.}$$

Moreover, the heat of absorption of hydriodic acid is found to be—

$$(HI, Aq) = 19,207 \text{ heat-units:}$$

hence, for the affinity of hydrogen for iodine in gaseous hydriodic acid we find—

$$(I, H) = - 6036 \text{ heat-units.}$$

4. *Oxygen.*—Direct combustion of oxygen in an atmosphere of dry hydrogen gave—

$$(H^2, O) = 68,357 \text{ heat-units,}$$

which is intermediate between the number determined by Andrews and that found by Favre & Silbermann (iii. 105).\*

5. *Sulphur.*—The affinity of sulphur and hydrogen was determined by the heat evolved on passing gaseous hydrogen sulphide into a solution of iodine in dilute hydriodic acid, in which iodine dissolves more freely than in pure water and without change of temperature. Experiment gave—

$$(I^2, Aq, SH^2) = 21,830 \text{ heat-units;}$$

\* The numbers in the table here referred to relate to the combustion of 1 gram (or one atom) of hydrogen; Thomsen's number to the combustion of 2 grams.

and since

$$(I, H, Aq) = 13,171 \text{ heat-units,}$$

we have for the affinity of sulphur to hydrogen—

$$(H^2, S) = 4,512 \text{ heat-units.}$$

Further, Thomsen has found for the heat of absorption of hydrogen sulphide in water—

$$(H^2S, Aq) = 4,754 \text{ heat-units :}$$

hence, the affinity of hydrogen for sulphur in aqueous solution is expressed by—

$$(H^2, S, Aq) = 9,266 \text{ heat-units.}$$

The number for the affinity of hydrogen to sulphur in gaseous hydrogen sulphide applies strictly only to sulphur in the state in which it separates from that combination, viz., as yellow, somewhat elastic sulphur, and would require a small correction to make it applicable to rhombic sulphur.

6. *Nitrogen*.—Every atom of chlorine passed into an aqueous solution of ammonia produces an evolution of heat represented by—

$$(NH^3, Aq, Cl) = 30,871 \text{ heat-units ;}$$

and as the neutralisation of hydrochloric acid by ammonia gives  $(HCl, Aq, NH^3, Aq) = 12,270$  heat-units, we obtain for the affinity between nitrogen and hydrogen in aqueous solution :

$$(N, H^3, Aq) = 35,142 \text{ heat-units ;}$$

but the heat of absorption of ammonia in water is—

$$(NH^3, Aq) = 8,435 \text{ heat-units ;}$$

therefore, by subtraction—

$$(N, H^3) = 26,707 \text{ heat-units.}$$

The mode of calculating the total heat of combination of the ammonium-compounds is indicated by the equation—

$$(NH^4, Cl, Aq) = (N, H^3, Aq) + (H, Cl, Aq) + (NH^3, Aq, HCl, Aq).$$

From his former determinations of the reactions on the right-hand side, Thomsen obtains—

$$(N, H^4, Cl, Aq) = 86,730 \text{ heat-units.}$$

$$(N, H^4, Br, Aq) = 75,790 \quad "$$

$$(N, H^4, I, Aq) = 60,580 \quad "$$

$$(N, H^4, S, Aq) = 50,600 \quad "$$

As also the latent heats of solution of the first three of these compounds are known, viz. :—

$$(NH^4Cl, Aq) = -3,880 \text{ heat-units.}$$

$$(NH^4Br, Aq) = -4,380 \quad "$$

$$(NH^4I, Aq) = -3,550 \quad "$$

the heats of combination of the ammonium-compounds in the solid state can be calculated—

$$(N, H^4, Cl) = 90,610 \text{ heat-units.}$$

$$(N, H^4, Br) = 80,170 \quad "$$

$$(N, H^4, I) = 64,130 \quad "$$

7. *Carbon*.—The affinity between hydrogen and carbon is calculated from the heat developed in the combustion of hydrocarbons. For marsh-gas and ethylene this amount of heat has been already several times determined. Thomsen has extended the investigation to acetylene.

a. *Marsh-gas*.—Since the heats of combustion of marsh-gas, as found by Dulong, Andrews, Favre, and Silbermann, do not differ much from each other, Thomsen adopts the mean of these determinations, viz. :—

$$(CH^4, O^4) = 209,900 \text{ heat-units ;}$$

from which the affinity of hydrogen and carbon is deduced by the equation—

$$(CH^4, O^4) = 209,900 \text{ heat-units} = (C, O^2) + 2(H^2, O) - (C, H^4).$$

Now Favre & Silberman found, for the heat of combustion of graphite (which may be regarded as the normal form of carbon) 7,800 heat-units per gram: consequently  $(C, O^2) = 12 \cdot 7800 = 93,600$  heat-units; and since, according to Thomsen,  $(H^2, O) = 68,357$ , it follows that

$$\begin{aligned}(C, H^4) &= (C, O^2) + 2(H^2, O) - (CH^4, O^2) \\ &= 93,600 + 136,714 - 209,900 \\ &= 20,414 \text{ heat-units.}\end{aligned}$$

*The affinity of carbon and hydrogen in marsh-gas is therefore positive.*

*β. Ethylene.*—The heat of combustion of this gas is, according to Thomsen's experiments,

$$(C^2H^4, O^2) = 334,800 \text{ heat-units;}$$

from which, by the equation

$$(C^2H^4, O^2) = 2(C, O^2) + 2(H^2, O) - (C^2, H^4),$$

there follows

$$(C^2, H^4) = -10,880 \text{ heat-units.}$$

*γ. Acetylene.*—The affinity of carbon and hydrogen in acetylene is calculated from its heat of combustion—

$$(C^2H^2, O^2) = 310,570 \text{ heat-units;}$$

from which, by the equation

$$(C^2H^2, O^2) = 2(C, O^2) + (H^2, O) - (C^2, H^2),$$

there follows

$$(C^2, H^2) = -55,010 \text{ heat-units.}$$

The affinity of hydrogen for every first member of the four natural groups of the non-metallic elements is positive, but diminishes for the members with greater atomic weights, and is even negative for some of the highest members, namely, for iodine, and according to Hautefeuille, for selenium (p. 616). Although no satisfactory explanation of this can be given at present, it must, at all events, be remembered that many thermo-chemical equations do not represent the actual physical conditions, inasmuch as they express the reactions of atoms upon each other instead of molecules. Thus, the heat of combustion of hydrogen in chlorine ought to be expressed, not by  $ClH = 22,001$  heat-units, but by  $(Cl^2, H^2) = 44,002$  heat-units, and the true value of the  $(Cl, H)$  can only be calculated from the equation  $(Cl^2, H^2) = 2(Cl, H) - (Cl, Cl) - (H, H)$ , in which the terms on the right-hand side are at present unknown.

From the reactions

$$\begin{aligned}(C^2, H^2) &= -55,010 \text{ heat-units,} \\ (C^2, H^4) &= -10,880 \text{ " } \\ (C, H^4) &= +20,420 \text{ " }\end{aligned}$$

it might appear that the affinity of carbon for hydrogen is negative. But as the hydrocarbons once formed produce a great amount of heat in their combination with more hydrogen, thus:—

$$\begin{aligned}(C^2, H^4) - (C^2, H^2) &= (C^2H^4, H^2) = +44,130 \text{ " } \\ 2(C, H^4) - (C^2, H^4) &= (C^2H^4, H^2) = +51,720 \text{ " }\end{aligned}$$

it can scarcely be doubted that the affinity of carbon for hydrogen is really positive, as, indeed, appears directly from the formation of marsh-gas.

The fact that the formation of the lower compounds of carbon with hydrogen and oxygen produces less heat than their combination with more hydrogen or oxygen, and that the direct combination of carbon with other elements can only be effected at very high temperatures, may perhaps be explained by the following hypothesis:—

*Carbon, as it is known as graphite, diamond, or charcoal, is in a negative or passive condition, out of which it must be brought before it can combine chemically with other elements, a certain amount of force being necessary to effect this transformation from the passive into the chemically active state.*

This force cannot at present be estimated, but amounts probably to about 70,000 heat-units for every carbon-atom.

*B. In the Combination of Oxygen with other Non-metallic Elements.*—*Formation of the Oxygen-acids of Sulphur* (Thomsen, *Dent. Chem. Ges. Ber.* v. 1014).—The following determinations relate to the affinities of sulphur and oxygen in the aqueous solutions of the several acids.

For the heat of absorption of sulphurous anhydride in water:

$$(SO^2, Aq) = 7,698 \text{ heat-units.}$$



For the oxidation of aqueous sulphurous acid by means of chlorine gas :

$$(\text{SO}^2\text{Aq}, \text{Cl}^2) = 73,907 \text{ heat-units.}$$

For the complete oxidation of sodium thiosulphate by hypochlorous acid in aqueous solution :

$$(\text{Na}^2\text{S}^2\text{O}^3\text{Aq}, 4\text{ClOH}, \text{Aq}) = 251,624 \text{ heat-units.}$$

For the action of iodine on a solution of sodium thiosulphate :

$$(2\text{Na}^2\text{S}^2\text{O}^3\text{Aq}, \text{I}^2) = 7,954 \text{ heat-units.}$$

For the decomposition of sodium thiosulphate by hydrochloric acid in aqueous solution :

$$(\text{Na}^2\text{S}^2\text{O}^3\text{Aq}, 2\text{HClAq}) = -2,176 \text{ heat-units.}$$

For the resolution of potassium dithionate in the dry way into potassium sulphate and sulphur dioxide :

$$(\text{K}^2\text{SO}^4, \text{SO}^2) = 0.$$

For the latent heat of sulphate and dithionate of potassium :

$$\begin{aligned} (\text{K}^2\text{SO}^4, \text{Aq}) &= -6,384 \text{ heat-units,} \\ (\text{K}^2\text{S}^2\text{O}^6, \text{Aq}) &= -12,986 \text{ "} \end{aligned}$$

To calculate from these numbers the relations of affinity of the sulphur acids, the following determinations, previously established by Thomsen, are required : relating to the thermic phenomena in the formation of water, of aqueous hydrochloric and hypochlorous acid (p. 606) ; in the neutralisation of sulphuric acid, &c. ; and, finally, in the reaction between 2 mol. hydrochloric acid and 1 mol. sodium dithionate in aqueous solution :

	Heat-units		Heat-units
(H <sub>2</sub> O)	68,357	(2NaHOAq, SO <sup>2</sup> Aq)	28,970
(I, H, Aq)	13,171	(2NaHOAq, S <sup>2</sup> O <sup>3</sup> Aq)	27,070
(Cl, H, Aq)	39,315	2(NaHOAq, HClAq)	27,480
(Cl, O, H, Aq)	28,322	2(NaHOAq, HIAq)	27,350
(NaHOAq, SO <sup>2</sup> Aq)	14,754	(NaHOSO <sup>2</sup> Aq, 2HClAq)	-978

Also, the heat of combustion of sulphur, as determined by Favre and Silbermann :

$$(\text{S}^2, \text{O}^2) = 71,072 \text{ heat-units.}$$

The calculation of the affinities in question is made from these numbers as follows :—

Since sulphurous acid in aqueous solution is converted by chlorine into sulphuric and hydrochloric acid, we have the equation :

$$(\text{SO}^2\text{Aq}, \text{Cl}^2) = (\text{SO}^2\text{Aq}, \text{O}) - (\text{H}^2\text{O}) + (\text{Cl}^2, \text{H}^2, \text{Aq}) ;$$

and therefore, according to the numbers above given,

$$(\text{SO}^2\text{Aq}, \text{O}) = 63,634 \text{ heat-units,}$$

and

$$(\text{SO}^2, \text{O}, \text{Aq}) = (\text{SO}^2\text{Aq}, \text{O}) + (\text{SO}^2, \text{Aq}) = 71,332 \text{ heat-units.}$$

From this follow the total heats of formation of sulphurous and sulphuric acids :

$$(\text{S}, \text{O}^2, \text{Aq}) = (\text{S}, \text{O}^2) + (\text{SO}^2, \text{Aq}) = 78,770 \text{ heat-units,}$$

and

$$(\text{S}, \text{O}^2, \text{Aq}) = (\text{S}, \text{O}^2) + (\text{SO}^2, \text{O}, \text{Aq}) = 142,404 \text{ heat-units.}$$

The decomposition of potassium dithionate in the dry way into sulphur dioxide and potassium sulphate, is not attended either with evolution or with absorption of heat : therefore

$$(\text{K}^2\text{SO}^4, \text{SO}^2) = 0, \text{ and } (\text{K}^2, \text{O}^2, \text{SO}^2) = (\text{K}^2, \text{O}^2, 2\text{SO}^2).$$

These reactions may be split up into

$$(\text{K}^2, \text{O}^2, \text{SO}^2) + (\text{K}^2\text{SO}^4, \text{Aq}) = (\text{K}^2, \text{O}, \text{Aq}) + (\text{SO}^2, \text{O}, \text{Aq}) + (2\text{KHOAq}, \text{SO}^2\text{Aq}),$$

and

$$(\text{K}^2, \text{O}^2, 2\text{SO}^2) + (\text{K}^2\text{S}^2\text{O}^6, \text{Aq}) = (\text{K}^2, \text{O}, \text{Aq}) + (2\text{SO}^2, \text{O}, \text{Aq}) + (2\text{KHOAq}, \text{S}^2\text{O}^6\text{Aq}).$$

On subtracting these two equations from each other, the first and third terms, being equal, disappear ; and all the remaining terms are known, except  $(2\text{SO}^2, \text{O}, \text{Aq})$ , which can therefore be calculated, viz. :

$$(2\text{SO}^2, \text{O}, \text{Aq}) = 68,950 \text{ heat-units.}$$

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We have then, for the total heat of formation of dithionic acid :

$$(S^2, O^4, Aq) = (2SO^2, O, Aq) + 2(S, O^2) = 211,094 \text{ heat-units.}$$

In the reaction of hypochlorous acid on sodium thiosulphate, 2 mol. of sulphuric acid are formed, together with 4 mol. of hydrochloric acid resulting from the deoxidation of the hypochlorous acid :

$$(Na^2S^2O^3Aq, 4ClOHAq) = \begin{cases} (S^2O^2Aq, O^4) \\ 2(NaHOAq, SO^2Aq, 2HClAq) - (2NaHOAq, S^2O^2Aq, \\ 4(Cl, H, Aq) - 4(Cl, O, H, Aq) \end{cases}$$

Now, according to the preceding data, the heat evolved in the reaction between 1 mol. sulphuric acid and 2 mol. hydrochloric acid with 1 mol. sodium hydrate is  $14,754 - 978 = 13,776$  units. The heat of neutralisation of thiosulphuric acid cannot be determined directly, on account of the instability of this acid ; but the decomposition of its sodium salt by hydrochloric acid is immediately attended with an absorption of heat amounting to 2,176 units, which indicates that the heat of neutralisation of thiosulphuric acid exceeds that of hydrochloric acid by about this number, and is therefore equal to about 29,656 units. As this number agrees nearly with the heat of neutralisation of sulphurous acid, viz. 28,970 units, it is assumed to be equal to the latter. The decomposition of the thiosulphuric acid into sulphur and sulphurous acid takes place gradually only, and is therefore without perceptible influence on the quantity 2,176. By introducing these values, together with those previously given, into the above equation, we obtain for the heat liberated in the oxidation of thiosulphuric to sulphuric acid,

$$(S^2O^2Aq, O^4) = 209,070 \text{ heat-units ;}$$

and by means of the equations

$$\begin{aligned} 2(S^2, O^2, Aq) &= (S^2, O^2, Aq) + (S^2O^2Aq, O^4) \\ (S^2, O^2, Aq) &= (S, O^2, Aq) + (SO^2, Aq, S) \end{aligned}$$

we obtain further :

$$\begin{aligned} (S^2, O^2Aq) &= 75,738 \text{ heat-units.} \\ (SO^2Aq, S) &= - 3,032 \text{ ,,} \\ (SO^2, S, Aq) &= + 4,666 \text{ ,,} \end{aligned}$$

for the heat-reactions implied in the formation of thiosulphuric acid.

The heat produced in the oxidation of thiosulphuric acid to *tetrathionic* acid can be calculated from the heat liberated in the reaction of iodine upon sodium thiosulphate :

$$2Na^2S^2O^3Aq, I^2 = \begin{cases} (I^2, H^2Aq) + 2(NaAq, HIAq) \\ (2S^2O^2Aq, O) - (O, H^2) \\ (2NaAq, S^4O^3Aq) - 2(2NaAq, S^2O^2Aq). \end{cases}$$

By assigning to these reactions their values, as given above (the neutralisation heat of tetrathionic acid is taken as equal to that of dithionic acid, 27,070 heat-units), we have

$$2(S^2O^2Aq, O) = 53,489 \text{ heat-units ;}$$

from which, by the equations

$$\begin{aligned} (S^4, O^3, Aq) &= 2(S^2, O^2, Aq) + (2S^2O^2Aq, O) \\ (S^4, O^3, Aq) &= 2(S, O^2) + (2SO^2, O, S^2, Aq), \end{aligned}$$

the affinities satisfied in the formation of tetrathionic acid are found :

$$(S^4, O^3, Aq) = 204,965 \text{ heat-units.}$$

If we consider thiosulphuric acid to be formed by the reaction of sulphurous acid, sulphur, and water, we obtain the effect of the second atom of sulphur by the equation :

$$(2SO^2, Aq) - (SO^2, S, Aq) = 7,698 - 4,666 = 3,032 \text{ heat-units,}$$

and considering tetrathionic acid to be formed in an analogous way from dithionic acid, we obtain the effect of the two additional atoms of sulphur from the equation—

$$(2SO^2, O, Aq) - (2SO^2, O, S^2Aq) = 68,950 - 62,821 = 6,129 \text{ heat-units.}$$

As  $6,129 = 2 \times 3,064$ , while the former difference was  $= 3,032$ , and as the calculations for thiosulphuric and dithionic acid are quite independent of each other, it follows that, for every additional atom of sulphur, the total heat of formation of the sulphur-acids is diminished by 3,032 to 3,064 heat-units.

It has not therefore been thought necessary to determine experimentally the heats of

formation of trithionic and pentathionic acids, as that of tetrathionic acid may be safely assumed to be about 3,064 units less than that of trithionic acid, and that of pentathionic acid about as much less than that of tetrathionic acid.

The heats of formation of the seven acids of sulphur are collected together in the following tables. Table I. shows the development of heat in the formation of the acids, from sulphur, oxygen, and water. Table II those which are obtained when the acids are derived from sulphurous anhydride.

TABLE I.

	Heat-units
(S, O <sup>2</sup> , Aq) . . . . .	= 78,770
(S <sup>2</sup> , O <sup>2</sup> , Aq) . . . . .	= 75,738
(S, O <sup>3</sup> , Aq) . . . . .	= 142,404
(S <sup>2</sup> , O <sup>3</sup> , Aq) . . . . .	= 211,094
(S <sup>3</sup> , O <sup>3</sup> , Aq) . . . . .	= 208,030
(S <sup>4</sup> , O <sup>3</sup> , Aq) . . . . .	= 204,965
(S <sup>5</sup> , O <sup>3</sup> , Aq) . . . . .	= 201,901

TABLE II.

	Heat-units
(SO <sup>2</sup> , Aq) . . . . .	= 7,698
(SO <sup>2</sup> , S, Aq) . . . . .	= 4,666
(SO <sup>2</sup> , O, Aq) . . . . .	= 71,332
(2SO <sup>2</sup> , O, Aq) . . . . .	= 68,950
(2SO <sup>2</sup> , S, O, Aq) . . . . .	= 65,886
(2SO <sup>2</sup> , S <sup>2</sup> , O, Aq) . . . . .	= 62,821
(2SO <sup>2</sup> , S <sup>3</sup> , O, Aq) . . . . .	= 59,757

If, in calculating the heat of formation of these acids, we take account also of the quantity evolved in the formation of the water contained in the hydrates, we obtain the values in Table III.

TABLE III.

	Heat-units
Sulphurous acid (SO <sup>2</sup> , O, H <sup>2</sup> , Aq) . . . . .	= 76,055
Thiosulphuric acid (SO <sup>2</sup> , S, O, H <sup>2</sup> , Aq) . . . . .	= 73,023
Sulphuric acid (SO <sup>2</sup> , O <sup>2</sup> , H <sup>2</sup> , Aq) . . . . .	= 139,869
Dithionic acid (2SO <sup>2</sup> , O <sup>2</sup> , H <sup>2</sup> , Aq) . . . . .	= 137,307
Trithionic acid (2SO <sup>2</sup> , S, O <sup>2</sup> , H <sup>2</sup> , Aq) . . . . .	= 134,243
Tetrathionic acid (2SO <sup>2</sup> , S <sup>2</sup> , O <sup>2</sup> , H <sup>2</sup> , Aq) . . . . .	= 131,178
Pentathionic acid (2SO <sup>2</sup> , S <sup>3</sup> , O <sup>2</sup> , H <sup>2</sup> , Aq) . . . . .	= 128,114

If we suppose the acids to be formed from sulphurous acid and hydroxyl, for which Thomsen has found—

$$(H^2, O^2, Aq) = 45,045 \text{ heat-units,}$$

we obtain for—

Sulphuric acid (SO <sup>2</sup> , Aq, H <sup>2</sup> , O <sup>2</sup> , Aq) . . . . .	= 86,946 heat-units.
Dithionic acid (2SO <sup>2</sup> , Aq, H <sup>2</sup> , O <sup>2</sup> , Aq) . . . . .	= 76,886 "

The corresponding values for every other polythionic acid with  $n$  sulphur-atoms may be found by subtracting  $(n-2)$  3,064 heat-units from that of dithionic acid.

C. *General Results.*—The results of the preceding investigations on the affinities of the elements, together with others obtained by similar methods, are collected in the following Tables. (*Deut. Chem. Ges. Ber.* vi. 1533.)

Reaction	Heat-units evolved or absorbed	Remarks
1. Hydrogen.		
Water . . . . .	(H <sup>2</sup> , O)	68,360
	Mol. Heat of volatilisation at 100°	9,660
	Mol. Heat of Fusion	1,440
Hydroxyl . . . . .	(H <sup>2</sup> , O <sup>2</sup> , Aq)	45,200
	(H <sup>2</sup> , O, O)	- 23,070
	( <sup>2</sup> O <sup>2</sup> , Aq, H <sup>2</sup> )	91,430
2. Chlorine.		
Hypochlorous acid	(Cl <sup>2</sup> , O)	- 18,040
	(Cl <sup>2</sup> , O, Aq)	+ 9,440
	(Cl <sup>2</sup> , O, Aq)	- 8,600
	(Cl, O, H, Aq)	+ 29,880
Chloric acid . . . . .	(ClOHAq, KOHAq)	+ 9,980
	(Cl <sup>2</sup> , O <sup>2</sup> , Aq)	- 20,480
	(Cl, O <sup>2</sup> , H, Aq)	+ 23,940
	(ClO <sup>2</sup> HAq, KOHAq)	+ 13,760
	(ClO <sup>2</sup> K, Aq)	- 10,040
	(KCl, O <sup>2</sup> )	- 9,760
	(HClAq, O <sup>2</sup> )	- 15,380
	(KClAq, O <sup>2</sup> )	- 15,370
		Gaseous acid Absorption of the gas by water

Reaction	Heat-units evolved or absorbed	Remarks
2. Chlorine.—Continued.		
Hydrochloric acid	$\begin{cases} (\text{Cl}, \text{H}) & + 22,000 \\ (\text{ClH}, \text{Aq}) & 17,320 \\ (\text{Cl}, \text{H}, \text{Aq}) & 39,320 \\ (\text{ClHAq}, \text{KOHAq}) & 13,750 \end{cases}$	Gaseous acid Absorption
3. Bromine.		
Bromic acid.	$\begin{cases} (\text{Br}^2, \text{O}^2, \text{Aq}) & - 43,520 \\ (\text{Br}, \text{O}^2, \text{H}, \text{Aq}) & + 12,420 \\ (\text{BrO}^2\text{HAq}, \text{KOHAq}) & 13,750 \end{cases}$	Heat of soln. of Br.
Hydrobromic acid	$\begin{cases} (\text{Br}^2, \text{Aq}) & 1,080 \\ (\text{BrHAq}, \text{O}^2) & - 15,960 \\ (\text{Br}, \text{H}) & + 8,440 \\ (\text{BrH}, \text{Aq}) & 19,940 \\ (\text{Br}, \text{H}, \text{Aq}) & 28,380 \\ (\text{BrHAq}, \text{KOHAq}) & 13,750 \end{cases}$	Gaseous acid
4. Iodine.		
Iodic acid	$\begin{cases} (\text{I}^2, \text{O}^2) & 41,960 \\ (\text{I}^2\text{O}^2, \text{Aq}) & - 1,900 \\ (\text{I}^2, \text{O}^2, \text{Aq}) & + 43,060 \\ (\text{I}, \text{O}^2, \text{H}) & 57,880 \end{cases}$	Anhydride Ditto Crystalline hydrate
Periodic acid	$\begin{cases} (\text{IO}^2\text{H}, \text{Aq}) & - 2,170 \\ (\text{I}, \text{O}^2, \text{H}, \text{Aq}) & 55,710 \\ (\text{IHAq}, \text{O}^2) & 42,540 \\ (\text{IO}^2\text{HAq}, \text{KOHAq}) & 13,810 \\ (\text{I}, \text{O}^2, \text{H}^2) & 185,780 \\ (\text{IO}^2\text{H}^2, \text{Aq}) & - 1,380 \\ (\text{I}, \text{O}^2, \text{H}^2, \text{Aq}) & + 184,400 \\ (\text{I}, \text{O}^2, \text{H}, \text{Aq}) & 47,680 \\ (\text{IHAq}, \text{O}^2) & 34,510 \\ (\text{I}^2, \text{O}^2, \text{Aq}) & 27,000 \\ (\text{IO}^2\text{H}^2\text{Aq}, \text{KOHAq}) & 5,150 \\ (\text{IO}^2\text{H}^2\text{Aq}, 2\text{KOHAq}) & 26,590 \end{cases}$	Cryst. hydrate $\left. \begin{matrix} \text{Ber. Ch. Ges. vi. 2} \\ \text{Gaseous acid} \end{matrix} \right\}$
Hydriodic acid	$\begin{cases} (\text{H}, \text{I}) & - 6,040 \\ (\text{HI}, \text{Aq}) & + 19,210 \\ (\text{H}, \text{I}, \text{Aq}) & 13,170 \\ (\text{HIAq}, \text{KOHAq}) & 13,680 \end{cases}$	
5. Sulphur.		
Sulphurous acid	$\begin{cases} (\text{SO}^2, \text{Aq}) & 7,700 \\ (\text{SO}^2, \text{Aq}) & 1,500 \\ (\text{S}, \text{O}^2) & 71,070 \\ (\text{S}, \text{O}^2, \text{Aq}) & 78,770 \\ (\text{SO}^2\text{Aq}, 2\text{NaOHAq}) & 28,970 \\ (\text{SO}^2, \text{O}) & 32,160 \end{cases}$	Gaseous acid Condensed acid Farre a. Silberm.  $\text{SO}^2$ becomes liquid anhydride
Sulphuric acid	$\begin{cases} (\text{SO}^2, \text{O}, \text{Aq}) & 71,330 \\ (\text{SO}^2\text{Aq}, \text{O}) & 63,630 \\ (\text{SO}^2, \text{O}^2, \text{H}^2) & 121,840 \\ (\text{SO}^2, \text{H}^2\text{O}) & 21,320 \\ (\text{SO}^2\text{H}^2, \text{Aq}) & 17,850 \\ (\text{SO}^2\text{Aq}) & 39,170 \\ (\text{S}, \text{O}^2) & 103,230 \\ (\text{S}, \text{O}^2, \text{H}^2) & 192,910 \\ (\text{S}, \text{O}^2, \text{H}^2, \text{Aq}) & 210,760 \\ (\text{SO}^2\text{Aq}, 2\text{NaOHAq}) & 31,380 \end{cases}$	$\text{SO}^2\text{H}^2$ becomes liquid hydrate  Liquid anhydride $\left. \begin{matrix} \text{Supposing that} \\ (\text{S}, \text{O}^2) = 71,070 \end{matrix} \right\}$

Reaction	Heat-units evolved or absorbed	Remarks	
5. Sulphur. — <i>Continued.</i>			
Dithionic acid	$\left\{ \begin{array}{l} (2\text{SO}^2, \text{O}, \text{Aq}) \\ (2\text{SO}^2\text{Aq}, \text{O}) \\ (\text{SO}^2\text{Aq}, \text{SO}^2\text{Aq}) \\ (\text{S}^2, \text{O}^2, \text{Aq}) \\ (\text{S}^2, \text{O}^2, \text{H}^2, \text{Aq}) \\ (\text{S}^2\text{O}^3\text{Aq}, 2\text{NaOHAq}) \end{array} \right.$	$\left\{ \begin{array}{l} + 68,950 \\ 53,550 \\ - 10,080 \\ + 211,090 \\ 279,450 \\ 27,070 \end{array} \right.$	$\left\{ \begin{array}{l} \text{If } \text{S}^2\text{O}^3\text{Aq is formed} \\ \text{If } (\text{S}, \text{O}^2) = \\ 71,070 \end{array} \right.$
Thiosulphuric acid	$\left\{ \begin{array}{l} (\text{SO}^2, \text{S}, \text{Aq}) \\ (\text{SO}^2\text{Aq}, \text{S}) \\ (\text{S}^2\text{O}^2\text{Aq}, \text{O}^4) \\ (\text{S}^2, \text{O}^2, \text{Aq}) \\ (\text{S}^2, \text{O}^2, \text{H}^2\text{Aq}) \end{array} \right.$	$\left\{ \begin{array}{l} - 1,570 \\ - 9,270 \\ 225,300 \\ 69,500 \\ 137,860 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \\ \text{If } (\text{S}, \text{O}^2) = 71,070 \end{array} \right.$
Tetrathionic acid.	$\left\{ \begin{array}{l} (2\text{SO}^2, \text{O}, \text{S}^2, \text{Aq}) \\ (2\text{SO}^2\text{Aq}, \text{O}, \text{S}^2) \\ (\text{S}^4, \text{O}^2, \text{Aq}) \\ (\text{S}^4, \text{O}^2, \text{H}^2, \text{Aq}) \end{array} \right.$	$\left\{ \begin{array}{l} 62,820 \\ 47,420 \\ 204,960 \\ 273,320 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \text{If } (\text{S}, \text{O}^2) = 71,070 \end{array} \right.$
Hydrogen sulphide	$\left\{ \begin{array}{l} (\text{S}, \text{H}^2) \\ (\text{SH}^2, \text{Aq}) \\ (\text{S}, \text{H}^2, \text{Aq}) \\ (\text{SH}^2\text{Aq}), \text{NaOHAq} \end{array} \right.$	$\left\{ \begin{array}{l} 4,510 \\ 4,750 \\ 9,260 \\ 7,740 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \text{Pogg. Ann. cxl. 522.} \end{array} \right.$
6. Selenium.			
Selenous acid	$\left\{ \begin{array}{l} (\text{Se}, \text{O}^2) \\ (\text{SeO}^2, \text{Aq}) \\ (\text{Se}, \text{O}^2, \text{Aq}) \\ (\text{SeO}^2\text{Aq}, 2\text{NaOHAq}) \end{array} \right.$	$\left\{ \begin{array}{l} 57,710 \\ - 920 \\ + 56,790 \\ 27,020 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Cryst. anhydride} \\ \\ \end{array} \right.$
Selenic acid	$\left\{ \begin{array}{l} (\text{Se}, \text{O}^2, \text{Aq}) \\ (\text{SeO}^2, \text{O}, \text{Aq}) \\ (\text{SeO}^2\text{Aq}, \text{O}) \\ (\text{SeO}^2\text{Aq}, 2\text{NaOHAq}) \end{array} \right.$	$\left\{ \begin{array}{l} 77,240 \\ 19,530 \\ 20,450 \\ 30,390 \end{array} \right.$	
7. Tellurium.			
Tellurous acid	$\left\{ \begin{array}{l} (\text{Te}, \text{O}^2, \text{H}^2\text{O}) \end{array} \right.$	$\left\{ \begin{array}{l} 81,190 \end{array} \right.$	
Telluric acid	$\left\{ \begin{array}{l} (\text{TeO}^2\text{Aq}, \text{O}) \\ (\text{Te}, \text{O}^2, \text{Aq}) \end{array} \right.$	$\left\{ \begin{array}{l} 25,850 \\ 107,040 \end{array} \right.$	
8. Nitrogen.			
Ammonia	$\left\{ \begin{array}{l} (\text{N}, \text{H}^3) \\ (\text{NH}^3, \text{Aq}) \\ (\text{N}, \text{H}^3, \text{Aq}) \\ (\text{NH}^3\text{Aq}, \text{HClAq}) \\ (\text{NH}^3\text{Aq}, \text{H}^2\text{S}, \text{Aq}) \\ (\text{N}, \text{H}^4, \text{Cl}, \text{Aq}) \\ (\text{N}, \text{H}^4, \text{Br}, \text{Aq}) \\ (\text{N}, \text{H}^4, \text{I}, \text{Aq}) \\ (\text{N}, \text{H}^4, \text{S}, \text{Aq}) \\ (\text{N}, \text{H}^4, \text{Cl}) \\ (\text{N}, \text{H}^4, \text{Br}) \\ (\text{N}, \text{H}^4, \text{I}) \\ (\text{NH}^3, \text{HCl}) \\ (\text{NH}^3, \text{HBr}) \\ (\text{NH}^3, \text{HI}) \end{array} \right.$	$\left\{ \begin{array}{l} 26,710 \\ 8,440 \\ 35,150 \\ 12,270 \\ 6,190 \\ 55,740 \\ 75,800 \\ 60,580 \\ 50,600 \\ 90,620 \\ 80,180 \\ 64,130 \\ 41,910 \\ 45,030 \\ 43,460 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Ammonia gas} \\ \\ \\ \\ \\ \\ \\ \\ \text{Cryst. salts} \\ \text{formed from the} \\ \text{gaseous con-} \\ \text{stituents} \end{array} \right.$
Nitrogen monoxide	$\left\{ \begin{array}{l} (\text{N}^2, \text{O}) \end{array} \right.$	$\left\{ \begin{array}{l} - 18,320 \end{array} \right.$	
Nitrogen tetroxide	$\left\{ \begin{array}{l} (\text{NO}, \text{O}) \\ (\text{NO}^2, \text{Aq}) \end{array} \right.$	$\left\{ \begin{array}{l} + 19,570 \\ 7,750 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Gaseous product} \end{array} \right.$
Nitric acid	$\left\{ \begin{array}{l} (2\text{NO}^2\text{Aq}, \text{O}) \\ (\text{N}^2\text{O}^2, \text{O}^2, \text{Aq}) \\ (\text{NO}^2, \text{O}, \text{H}, \text{Aq}) \end{array} \right.$	$\left\{ \begin{array}{l} 18,300 \\ 72,040 \\ 51,080 \end{array} \right.$	

Reaction	Heat-units evolved or absorbed	Remarks	
9. Carbon.			
Carbon monoxide and dioxide	(CO, O)	66,810	Favre & Silbermann, for wood-charcoal If (C, O <sup>2</sup> ) = 96,960
	(CO <sup>2</sup> Aq)	5,880	
	(CO, O, Aq)	72,690	
	(C, O <sup>2</sup> )	96,960	
Marsh gas, ethylene, and acetylene	(CO)	30,150	If (C, O <sup>2</sup> ) = 96,960
	CH <sup>4</sup> , O <sup>4</sup>	4 . 52,480	
	C <sup>2</sup> H <sup>4</sup> , O <sup>8</sup>	6 . 55,800	
	C <sup>2</sup> H <sup>2</sup> , O <sup>3</sup>	5 . 62,110	
	C <sub>2</sub> H <sup>4</sup>	23,760	
	C <sup>2</sup> , H <sup>4</sup>	— 4,160	
	C <sup>2</sup> , H <sup>2</sup>	— 48,270	

D. *The Common Constant of Affinity.*—A comparison of the quantities of heat evolved in a large number of chemical reactions leads to the conclusion, that these quantities, and therefore also the forces of affinity which they measure, are multiples of a common constant, the value of which is about 18,000 heat-units. The following numbers exhibit this reaction in two series of chemical processes:

$(\text{N}^2\text{O}^2, \text{O}, \text{Aq})$	=	2. 18,170 heat-units
$(\text{N}^2\text{O}^2, \text{O}^2, \text{Aq})$	=	3. 18,214 "
$(\text{N}^2\text{O}^2, \text{O}^2, \text{Aq})$	=	4. 18,235 "
$(\text{Cu}, \text{O}, \text{SO}^2\text{Aq})$	=	3. 18,075 "
$(\text{Pb}, \text{O}, \text{SO}^2\text{Aq})$	=	4. 18,888 "
$(\text{Fe}, \text{O}, \text{SO}^2\text{Aq})$	=	5. 18,772 "
$(\text{Cd}, \text{O}, \text{SO}^2\text{Aq})$	=	3. 18,094 "
$(\text{Zn}, \text{O}, \text{SO}^2\text{Aq})$	=	6. 18,077 "
$(\text{Mg}, \text{O}, \text{SO}^2\text{Aq})$	=	10. 18,092 "

In these two series the character of the chemical reaction is perfectly analogous for the members of each; the former representing the formation of the oxygen-acids of nitrogen from nitrogen dioxide, oxygen and water, the latter that of metallic sulphates from metal, oxygen, and sulphuric acid.

The conversion of aqueous chlorine into hydrochloric acid with decomposition of water, gives the thermic relation:

$$(\text{Cl}^2\text{Aq}, \text{H}^2) - (\text{H}^2, \text{O}) = 5,403 \text{ heat-units};$$

whence, since  $(\text{H}^2, \text{O}) = 6,836$  h. u., we find for the conversion of chlorine-water into hydrochloric acid, by direct addition of hydrogen  $(\text{Cl}^2\text{Aq}, \text{H}^2) = 73,764$  h. u.; and in like manner may be calculated the quantities of heat which would be evolved in the conversion of aqueous solutions of bromine and hydroxyl into water by direct addition of hydrogen. The result is as follows:—

$(\text{Br}^2\text{Aq}, \text{H}^2)$	=	55,654 = 3. 18,551 heat-units
$(\text{Cl}^2\text{Aq}, \text{H}^2)$	=	73,764 = 4. 18,441 "
$(\text{H}^2\text{O}^2\text{Aq}, \text{H}^2)$	=	91,675 = 5. 18,335 "

A similar group of processes is exhibited by the action of chlorine on solutions of ferrous chloride, stannous chloride, and sulphurous acid also on mercury and cuprous chloride suspended in water:

$(\text{Hg}^2\text{Cl}^2, \text{Aq}, \text{Cl}^2)$	=	37,075 = 2. 18,537 heat-units
$(2\text{FeCl}^2, \text{Aq}, \text{Cl}^2)$	=	54,810 = 3. 18,270 "
$(\text{SnCl}^2, \text{Aq}, \text{Cl}^2)$	=	73,875 = 4. 18,469 "
$(\text{SO}^2\text{Aq}, \text{Cl}^2)$	=	73,907 = 4. 18,477 "

These numbers show that the common constant of affinity has the same value, whether the element which enters into combination be oxygen, hydrogen, or chlorine.

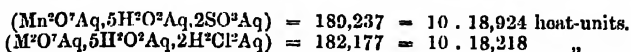
A similar relation is exhibited by the quantities of heat evolved in the following reactions:—

$(2\text{FeSO}^4\text{Aq}, \text{O}, \text{SO}^2\text{Aq})$	=	36,800 = 2. 18,400 heat-units
$(2\text{CrO}^3\text{Aq}, 3\text{SO}^2\text{Aq})$	=	36,884 = 2. 18,442 "
$(\text{Mn}^2\text{O}^4\text{Aq}, 2\text{SO}^2\text{Aq})$	=	72,647 = 4. 18,162 "

The first of these reactions, in which ferrous sulphate is converted into ferric sulphate by oxygen and sulphuric acid, is perfectly analogous to the conversion of ferrous into ferric chloride by the action of chlorine; and the quantities of heat evolved in the two reactions are as 2 : 3. In the two other processes, chromic and permanganic acids

are converted by sulphuric acid into the normal sulphates of chromium and manganese, with evolution of oxygen. The quantities of heat evolved are as 2:4, and the common constant is the same as before.

When hydrogen dioxide and permanganic acid act on one another in presence of a free acid, sulphuric or hydrochloric acid, for example, 5 mol. of oxygen are evolved for each molecule of permanganic acid decomposed, the products of the reaction being water and manganous sulphate or chloride. The thermic effects of the two reactions are:



10 atoms or 5 mol. of oxygen are given off, and the quantity of heat developed amounts to 10 times the value of the common constant.

The mean value of the common factor in the twelve reactions above cited, in which hydrogen, chlorine, sulphuric acid, and hydrogen dioxide are the reagents common to the several groups, is 18,427 heat-units; and the mean value for the nine processes in which oxygen is the common reagent, is 18,361 heat-units. It may therefore be inferred that, allowing for unavoidable errors of observation, the actual value of the constant of affinity is the same in all these cases (Thomson, *Deut. Chem. Ges. Ber.* vi. 239).

E. Development of Heat in the Combination of Hydrogen with the various Modifications of Sulphur and Selenium.—Hautefeuille (*Compt. rend.* lxxviii. 1554) has determined the quantities of heat evolved in the combination of hydrogen with sulphur and selenium in their various molecular states. The mode of experimenting consisted in decomposing hydriodic acid gas with sulphur and selenium at ordinary temperatures within a mercury calorimeter. According to Favre, 1 mol. hydriodic acid, in separating into free hydrogen and solid iodine, evolves 6,840 units of heat. Now Hautefeuille finds that the substitution of 1 atom of octohedral sulphur for iodine ( $2\text{HI} + \text{S} = \text{H}^2\text{S} + \text{I}^2$ ) develops 13,680 heat-units. Consequently, in the combination of 1 atom octohedral sulphur with hydrogen there are evolved  $13,680 - 2 \cdot 4,430 = 4,820$  units of heat. Moreover, the heat of combustion of 1 atom of hydrogen is 34,462 units (iii. 105), and that of 1 atom of octohedral sulphur is 71,968 units; therefore the heat of combustion of 34 grams of hydrogen sulphide is:

$$2 \cdot 34,462 + 71,968 - 4,820 = 136,072 \text{ heat-units.}$$

The direct oxidation of hydrogen sulphide by means of hypochlorous acid, gave a somewhat higher number, viz., 136,400; but this reaction is complicated by the formation of sulphur chloride, which oxidises but slowly.

The conversion of 1 atom of insoluble into crystallised sulphur is attended, according to Favre, with the absorption of 6,204 units of heat. Consequently, in the decomposition of hydrogen sulphide into hydrogen and insoluble sulphur, there are absorbed  $6,104 - 4,820 = 1,284$  units of heat; and in the combination of hydrogen with insoluble sulphur, effected by means of hydriodic acid,  $13,680 - 6,104 = 7,476$  units are evolved. Direct experiment gave a larger number, but still below 8,860; the difference is attributed by Hautefeuille to the difficulty of preparing insoluble sulphur in the pure state.

The development of heat which takes place in the preparation of hydriodic acid by hydrogen sulphide and iodine is due, partly to the solution of the hydrogen sulphide in water, partly to the chemical reaction. Estimating the heat of solution of 1 mol. hydrogen sulphide in water at 6,750 units, it is found that 1 mol. of this dissolved acid, on decomposing in the manner above mentioned, evolves 24,000 heat-units. The hydriodic acid (2 mol.) thereby produced contains, in the dilute state, according to Favre, 28,950 heat-units less than its elements; and the whole of this quantity of heat must have been set free if the dissolved hydrogen sulphide had decomposed without absorption of heat. The 4,950 units thus absorbed represent the quantity of heat which would be developed in the direct combination of hydrogen with the undetermined variety of sulphur which is obtained by precipitating this element from a solution of hydrogen sulphide.

The evolution of heat in the formation of hydriodic acid becomes less as the concentration of the solution is greater. The reaction will go on, attended with evolution of heat, so long as the solution of hydriodic acid has not attained the degree of concentration at which it loses the quantity of heat which is required for the decomposition of the hydrogen sulphide in aqueous solution, that is to say, about 11,650 units. It is a question whether, at a higher degree of concentration, the reverse action would take place. Under pressure this seems to be the case; otherwise concentrated hydriodic acid acts upon sulphur only when gaseous acid is evolved in consequence of elevation of temperature.

The evolution of heat in the combination of selenium with hydrogen may be determined in a similar manner. The decomposition of gaseous hydriodic acid by red selenium and by metallic selenium, is attended with only a very slight evolution of heat. 1 mol. hydrogen selenide, in resolving itself into hydrogen and metallic selenium, would give out 5,400 heat-units; if it were resolved into hydrogen and red selenium, it would evolve 4,280 units. Consequently, the combination of hydrogen with these two modifications of selenium must be attended with absorption of heat. Hydrogen selenide is likewise decomposed by iodine, with separation of red selenium, which then unites with the excess of iodine (Hautefeuille).

A. Naumann (*Deut. Chem. Ges. Ber.* ii. 177) finds that hydrogen sulphide does not act at ordinary temperatures on iodine dissolved in dehydrated carbon sulphide, or on solid or aqueous iodine in the absence of water. A solution of iodine in carbon sulphide saturated with hydrogen sulphide does not lose the odour of that gas by keeping; but when shaken with water it makes the water turbid by separation of sulphur. This behaviour of iodine to hydrogen sulphide is explained by the thermic relations of the two substances. The reaction represented by the equation  $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S}$ , which is intended merely to exhibit, in their simplest form, the quantitative relations of the bodies present before and after the chemical change, requires an absorption of  $5,480 + 2 \cdot 3,600 = 12,620$  units of heat (iii. 115). It cannot, therefore, take place independently at ordinary temperatures. That it takes place in presence of water is due to the fact, that the dissolution of the hydriodic acid produced ( $2\text{HI}$ ) gives rise to the evolution of 37,800 heat-units (iii. 113;  $147 \cdot 7 \times 128 \times 2 = 37,811$ ). The total evolution of heat is therefore  $37,800 + x - 12,680 = 25,120 + x$ , where  $x$  denotes the negative heat of solution of iodine alone, taken with a positive sign. But it is found that the heat developed by the absorption of equal quantities of hydriodic acid gas is less as the quantity of that acid already dissolved in the water is greater. The positive sum of the quantities of heat evolved must therefore diminish as the quantity of hydriodic acid in the liquid increases, until the positive and negative evolutions of heat neutralise one another, and the total evolution is reduced to nothing. The inference thence deducible, that the mutual action of iodine and hydrogen sulphide goes on in presence of water will reach its limit at a certain degree of concentration of the resulting solution of hydriodic acid, at which gaseous hydriodic acid must be dissolved with absorption of heat, is fully verified by experiment. The limit of concentration in question corresponds with a specific gravity of 1.56 at ordinary temperatures referred to water at the same temperature; whereas the acid which distils over at  $127^\circ$ – $128^\circ$  under the ordinary atmospheric pressure has a specific gravity of 1.67 (*1st Suppl.* 738), and a solution saturated at  $0^\circ$  a specific gravity of 1.99. Aqueous hydriodic acid of specific gravity 1.56 absorbs hydriodic acid gas passed into it, with considerable rise of temperature.

F. *Heat of Combination of Iodine with Oxygen*.—A. Ditte (*Ann. Chim. Phys.* [4] xxi. 52) has determined the heat of combustion of iodine in oxygen by means of the formation of phosphoric acid resulting from the action of iodine on red phosphorus (see Iodic Acid); also the heat of solution of iodic anhydride and iodic acid, and the heat of contraction of iodic acid from the corresponding densities, expansion-coefficients, and specific heats, whence also the heat of combination of iodic acid with water is deduced:

	Heat-units	
	For 1 gram	For 1 mol.*
Heat of Combination of Iodine ( $\text{I}_2$ ) to Iodic Anhydride	+ 110.00	+ 2792.0
Heat of Solution of Iodic Anhydride $\text{I}_2\text{O}_5$	— 5.7	— 1902.4
Heat of Solution of Iodic acid $\text{HIO}_3$	— 12.7	— 2240.6
Heat of Contraction of Iodic acid	+ 0.45	+ 1135.7
Heat of Combination of Iodic Anhydride ( $\text{I}_2\text{O}_5$ ) with Water	+ 0.6	+ 307
Specific Heat of Iodic acid	0.1625	

G. *Heat of Combination of Boron and Silicon with Chlorine and Oxygen* (Troost & Hautefeuille, *Compt. rend.* lxx. 185, 252).—The experiments, made with a mercury calorimeter, gave the following results:—

*Amorphous Boron.*

	Heat-units	
	For 1 gram	For 1 atom
In Combination with Oxygen	14,420	158,600
In Combination with Chlorine	9,455	104,000
In the action of Boron Chloride on 140 times its weight of Water	7,200	79,200

\* This number differs widely from Thomsen's (p. 619).



*Amorphous Silicon.*

	For 1 gram	For 1 atom	
		Si=28	Si=21
In Combination with Oxygen . . . . .	7,830	219,240	164,430
In Combination with Chlorine . . . . .	5,630	157,640	118,230
In the action of Silicon Chloride on 140 times its weight of Water . . . . .	2,915	81,640	61,220
In the Isomeric Transformation of Amorphous into Crystallised Silicon . . . . .	290	8,120	6,090

H. *Heat of Oxidation of Magnesium, Cadmium, Indium, and Zinc* (A. Ditte, *Compt. rend.* lxxii. 762, 858; lxxiii. 108).—The determinations were made in the mercury-calorimeter by two methods. In the first, equivalent weights of the metal and of its oxide were dissolved in sulphuric acid, and the quantities of heat thereby evolved were determined. The difference of these two numbers gives the quantity of heat produced when the metal is oxidised at the expense of hydrogen, and by combining this result with the known heat of combustion of hydrogen itself, the heat developed by the direct combustion of the metal can be calculated. In the second method, the heats of solution of the metal and of its oxide in iodic acid were determined. Now 1 eq. of the metal in passing to the state of iodate decomposes  $\frac{1}{2}$  eq. iodic acid, whereby 2,792 units of heat are expended, and from this the heat of combustion of the metal may be calculated. For magnesium both methods were used; for zinc and indium, the first; for cadmium, the second. The following are the mean values of the heats of combustion obtained:—

	Equivalent	Heat of Combustion	
		for 1 gram	for 1 eq.*
Magnesium . . . . .	12	6130.5	73,566 heat-units
Zinc . . . . .	32.5	1357.6	44,122 "
Indium . . . . .	37.8	1044.6	39,486 "
Cadmium . . . . .	56	271.1	15,182 "

The difference between the number found by Ditte for zinc and the number 42,451 determined by Favre & Silbermann arises from the difference in the heat of solution of oxides according to the temperatures to which they have been previously raised. For zinc oxide, Ditte found the following thermic effects on solution in dilute sulphuric acid, according to the temperature to which the zinc hydrate had been previously heated:—

Temperature	for 1 gram	for 1 equiv.
350° . . . . .	244.2	9,890 heat-units
Dark red heat . . . . .	272	11,016 "
Bright red heat . . . . .	299.7	12,138 "

This marked effect of temperature alone on the properties of a body is shown by the experiments with magnesia cited in the following table, where T denotes the temperature of ignition, D<sub>o</sub> the density of the ignited oxide,  $\alpha$  its expansion-coefficient for 1° between 0° and 100°; Q<sub>1</sub> the heat of solution of 1 eq. magnesia in dilute sulphuric acid; D<sub>h</sub> the density of the hydrate reproduced by moistening the calcined magnesia with water; Q<sub>2</sub> the heat of solution, in gram-degrees, of 1 eq. of this hydrate:—

T	D <sub>o</sub>	$\alpha$	Q <sub>1</sub>	D <sub>h</sub>	Q <sub>2</sub>
350° . . . . .	3.1932	0.0003104	16,655	2.3261	14,244
440° . . . . .	3.2014	0.0002402	18,417	2.3631	14,431
Dull red heat . . . . .	3.2482	0.0001764	19,234	2.6040	18,340
Bright red heat . . . . .	3.5699	0.0001634	20,094		

These numbers show that after strong ignition, the rate of expansion diminishes while the density and the development of heat attending combination with sulphuric acid increase. This last result is contradictory to the generally received opinion that the quantity of heat in a body diminishes as its density increases.

Ditte (*Compt. rend.* lxxiii. 272) has also determined the heat of combination of cadmium oxide in two modifications with dilute sulphuric acid (382.5 grams in a litre).

	For 1 gram	For 1 eq.
Black crystallised oxide (obtained by igniting the nitrate)	229.6	14,238
Orange-coloured amorphous oxide (obtained by igniting the carbonate or by combustion of the metal)	234.1	14,513

\* To find the quantities of heat evolved in the combustion of an atom of each of these metals, the number for indium must be multiplied by 3, those for the other metals by 2.

Marignac (*Archives des Sciences* [2], xliii. 209) has also determined the heat of solution of magnesia and zinc oxide, after calcination, at different temperatures, in dilute sulphuric acid, and has arrived at conclusions different from those of Ditte. The acid diluted with 25 eq. water and having a sp. gr. of 0.8637 was contained in a cylindrical metallic vessel whose heat-capacity was equivalent to 6 grams of water; this vessel was suspended within an iron cylinder surrounded by water at the temperature of the room. After the temperature of the acid had become constant, a weighed quantity of the oxide was introduced. A thermometer divided into  $\frac{1}{10}$  of a degree was used as a stirrer and indicated the rise of temperature, which was in all cases read off four minutes after the introduction of the oxide. The dissolution of the oxides, which were finely divided and added in small quantities (not exceeding 1.2 gram), was complete in two or three minutes. Taking account of the circumstance that magnesium nitrate and magnesium hydrate cannot be completely freed by heating from nitric acid and water respectively, the means of several experiments give the following relative values:—

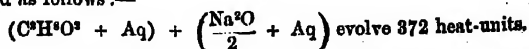
				Gram-degrees
1 gram of Magnesia heated to 440				874
"	"	"	dull redness	875
"	"	"	bright redness	867
"	Zinc oxide	"	350°	261
"	"	"	dull redness	266
"	"	"	bright redness	264

From the first three values, Marignac does not think himself justified in concluding that the heat of solution of magnesia is diminished by previous strong ignition, since the differences fall within the limits of probable experimental error; but he regards them as showing at least that no increase takes place. The three values for zinc oxide likewise do not exhibit any appreciable alteration in the heat of solution, the somewhat smaller number obtained at 350° being probably due to a residue of 0.5 pc. of water. As the most probable absolute values of the heat of solution of 1 gram of the oxides in dilute sulphuric acid, Marignac gives for magnesia 905, and for zinc oxide 275 gram-degrees. He is of opinion that Ditte's observations are affected by an error arising from the calorimetric method employed.

**Thermal Effects of the Combination of Alcohols with Bases.**—Borhelot (*Compt. rend.* lxxiii. 663) has examined the thermal effects of the combination of bases with alcohols, phenols, and aldehydes, and with some compounds which, like silicic acid, have a character intermediate between acids and alcohols, with the view of throwing some light upon the chemical character of these bodies. The calorimeters used were of platinum, holding about 600 cubic centimeters up to 1 litre and 2.25 litres of liquid; these were placed within a vessel having several concentric walls, some of which were lined with silver-plate, the rest with tin-plate. The external compartment, which was very large, was filled with water several days before the experiment. The thermometers used indicated differences of temperature within  $\frac{1}{100}$  of a degree. When the liquids operated upon contained half an equivalent, which was most frequently the case, they were called normal solutions, but sometimes they contained only one-quarter of an equivalent in 1 litre.

**Ethyl Alcohol.**—It is well known that the alcoholates of barium, potassium, sodium, are decomposed, gradually at least, by water; and that the presence of an excess of water does not permit their existence is shown by mixing a solution of alcohol (32 grams in 1 litre) with a solution of potash (20.2 grams of  $K^2O$  in 1 litre). The rise of temperature observed was .005°, which is so small that it falls within the errors of experiment, and may be neglected. Also, if the water be added after the mixing of the alcohol and the potash (160H<sup>2</sup>O for C<sup>2</sup>H<sup>5</sup>O), the formation of the alcoholate is completely stopped, whilst with this degree of dilution the polyatomic alcohols still manifest their affinity for the alkalis.

**Glycerin.**—The thermal reaction taking place when the normal solutions are mixed is expressed as follows:—



The dilution of the resulting mixture with five times its volume of water produces an absorption of 363 heat-units. The heat evolved on mixing being nearly equal to that absorbed on diluting, it may be concluded that the compound formed in the first reaction is destroyed by the addition of so much water.

Further experiments showed that more heat is evolved on adding more glycerin, as well as on adding more soda to a solution of glycerin containing 100 grams in a litre.

These experiments lead to the following general conclusions:—

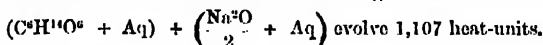
1. The reaction of glycerin upon the alkalis produces heat, not excooling, in the case of the normal solutions, the  $\frac{1}{30}$ th part of the heat evolved by the combination of an acid with a base.

2. The heat increases with the number of equivalents of glycerin added to 1 equivalent of sodium hydrate, and *vice versa*, without being proportional to the quantities added, either of the one or the other compound.

3. The heat diminishes as the dilution becomes greater, and none at all is evolved in the presence of 1200 H<sup>2</sup>O. In short the compound formed in a concentrated solution is decomposed, with absorption of heat, on the addition of a sufficient quantity of water.

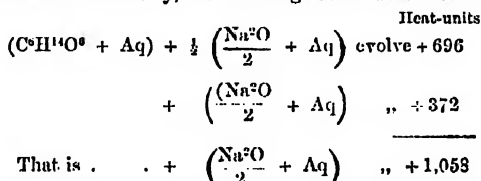
These phenomena, particularly the continual division of the base between the alcohol on the one and the water on the other side, may be considered as characterising in general, and almost numerically, the combination of bases with alcohols; they differ from the phenomena attending the combination of bases with true acids, inasmuch as the neutral salts of the latter are formed in fixed proportions, and are not destroyed by the addition of any amount of water.

*Mannite*.—The thermic reaction observed on mixing the normal solutions was—

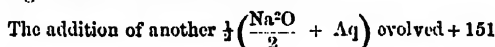


The heat, although much more considerable than in the case of glycerin, is still only the  $\frac{1}{10}$ th part of the heat of combination of the true acids.

On adding the soda successively, the following results were obtained:—



which value agrees with the first determination.



Total .. + 1,209

The evolution of heat does not, therefore, increase proportionately to the weight of sodium hydrate added.

The absorption of 1,430 heat-units observed on diluting the solution obtained in this experiment, proved the decomposition of the compound formed in the concentrated liquid.

The reaction  $(C^6H^{14}O^8 + Aq) + \left(\frac{K^2O}{2} + Aq\right)$  produced 1,145 h. u., that is to say, almost the same as when sodium hydrate is taken.

Lime in its reaction with mannite was found to be thermically equivalent to potash or soda.

In general, whether an alcohol combines with an acid to form an ether, or with a base to form an alcoholate, it appears that the amount of combination taking place always depends upon the quantity of water present, which itself exhibits a strong tendency to combine with the acid or base.

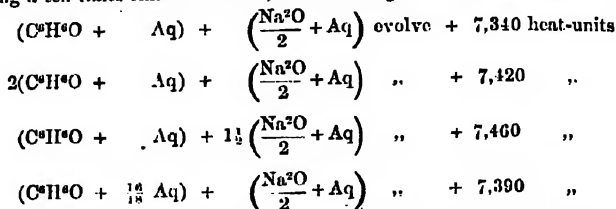
Although in the reactions of etherification, equilibrium is obtained after a considerable time only, while the formation and decomposition of the alcoholates in the presence of water seems to be instantaneous, it appears, notwithstanding this difference, that the combination of alcohols with acids, as well as with bases, obeys laws of chemical statics which, though less general but more simple, predominate in the formation of neutral salts.

*Gum*.—300 c. c. of a solution of 1 part of gum in 100 parts of water were mixed with 134 c. c. of a solution of soda (24.6 per litre).

The heat evolved was	+ 132 units
The addition of 137 c. c. of soda-solution produced	+ 29 „
Finally, the addition of other 39 c. c. produced	+ 6 „
	+ 167 „

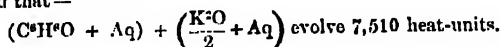
The heat absorbed on adding 5 volumes of water to the mixture was -174 units, which, differing very little from the heat of combination, indicates an almost complete decomposition of the compound at first formed.

*Phenol*.—100 parts of water dissolve 1 part and more of crystallised phenol, 2,075 heat-units being absorbed during the solution of every 94 grams (the molecular weight) of phenol. When a solution of this strength acts upon an equivalent solution of soda occupying a ten times smaller volume, the following reactions are observed:—



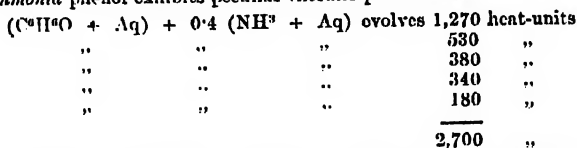
These numbers show, 1st, that only *one* phenate of sodium is formed; 2nd, that the evolution of heat is independent of the quantity of water present; and that, for these reasons, phenol, in accordance with other properties already known, seems to act towards the alkalis like one of the true acids, from which it differs by having only half as great a heat of combination.

It was found that—



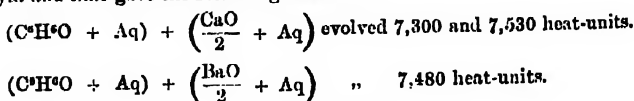
On adding the potash in successive portions, the heat increased proportionately to the quantity of base added.

With *ammonia* phenol exhibits peculiar thermic phenomena:—



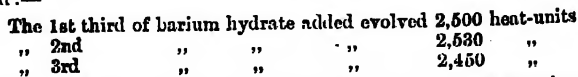
These numbers show that the heat evolved on adding ammonia in successive portions to phenol is not proportional to the quantity added, being greater for the earlier than for the later portions. This result is attributed by Berthelot to the partial decomposition of ammonium phenate by water.

Baryta and lime gave the following results:—



No more heat is produced by an excess of base.

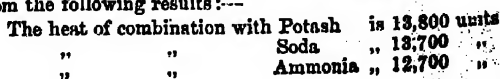
The following reactions show that the heat evolved is in proportion to the weight of base added:—



The phenates of the alkali-metals yield their total heat of combination at the moment of their formation.

The fact that the amount of heat evolved by the combination of the hydrates of potassium, sodium, barium, and calcium with phenol is very nearly the same, and that it is scarcely influenced by the greater or smaller quantity of water present, strengthens the conclusion arrived at before, as to the close relationship of phenol to the true acids.

*Trinitrophenol*, or *Picric Acid*.—That picric acid possesses the character of a true acid is shown from the following results:—



The addition of a second equivalent of soda produces no more heat. The behaviour of ammonia, on being added by successive thirds, is illustrated by the following table:—

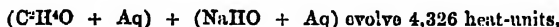
The 1st third of an equivalent of ammonia added evolved	4,240 heat-units
" 2nd " " "	4,200 "
" 3rd " " "	4,270 "
" 4th " " "	— "
	<hr/>
	12,710 "

It appears, then, that neither an acid nor a basic ammonium salt can have been formed.

The heat absorbed during the solution of picric acid was found = 7,000 units.

*Aldehyde.*—The solution of 1 mol. of aldehyde in water produces 3,620 heat-units, three-fourths of which are evolved almost instantaneously, whilst several minutes are required for the liberation of the remaining fourth. This large evolution of heat seems to indicate the formation of a definite compound, with a constitution perhaps resembling that of the hydrate of chloral.

On mixing equivalent solutions of aldehyde and of sodium hydrate, it was found that

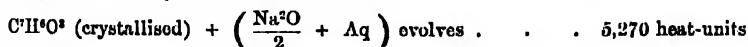


which is about one-third part of the heat of combination of the true acids.

Here, also, a little more than half of the heat is given off at once, whilst the second half requires four or five minutes. Dilution of the mixture obtained with five times its volume of water causes an absorption of 1,510 heat-units, indicating a decomposition, at least partial, of the compound at first formed. It appears, therefore, that aldehyde partakes of the character of an acid as well as of a base; the combination with water, however, and the evolution of the heat of combination in successive unequal quantities, are phenomena peculiar to aldehyde.

*Alcoholic acids.*—1. *Salicylic.* The first of these compounds behaves as a monobasic acid and as an acid alcohol at the same time. The heat evolved on mixing a solution of salicylic acid with a solution of sodium hydrate is 14,600 units, which number agrees with its first character.

When a second equivalent of soda-solution is added, the liquid becomes too dilute for the exhibition of any sensible increase of heat.

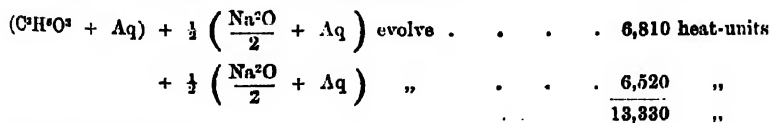


On addition of a second equivalent of soda evolves . . . 2,000 "

Then, on dilution with a five-fold volume of water . . . -2,050 "

whence it appears that the bibasic salicylate is decomposed by a large quantity of water, whereas the monobasic salt is independent of the quantity of water present.

2. *Lactic acid*,  $C^3H^5O^3$ .—1 equivalent (= 90 grams) was dissolved in 2 litres of water and half an equivalent of soda in 1 litre of water:—



In another experiment . . . 13,440 "

On further addition of 1 eq. soda . . . 210 "

Then, on dilution with 5 vol. water . . . 70 "

3. *Tartaric acid*,  $C^4H^4O^6$ .—



On dilution with an equal volume of water . . . -35 "

Therefore, in the union of the neutral tartrate with soda . . . +30 "

It appears, then, that the alcoholic acids exhibit their double function by the quantities of heat developed in their combination with bases. Their acid character shows itself in all cases by the evolution of a quantity of heat proportional to the quantity

of base added, and independent of the quantity of water present so long as a neutral salt is being formed. The alcoholic character, on the other hand, is exhibited especially in the action of bases in very concentrated solutions, and by the rapid diminution of the thermic effects on dilution with water.

**Thermic Relations of the Cyanogen Compounds** (Berthelot, *Compt. rend.* lxxiii. 448).

1. *Hydrocyanic acid*.—A known weight of the acid was decomposed by very strong hydrochloric acid, the mixture was diluted with water after the reaction was completed, and the evolution of heat determined:

	Heat-units
HCN (pure and liquid) + HCl (dilute) + 2H <sup>2</sup> O = CH <sup>2</sup> O <sup>2</sup> (dissolved)	
+ NH <sup>4</sup> Cl (dissolved) . . . . .	gave +10,000
and	
C + H + N = CNH (pure and liquid) . . . . .	—37,700

The same acid on dissolving in water may evolve or absorb heat, according to circumstances. With a large quantity of water 400 units are evolved. The heat of volatilisation of HCN is 5,700 units. Hence:

	Heat-units
Formation of the dissolved acid from its elements . . . . .	— 37,300
Heat of combustion of liquid hydrocyanic acid . . . . .	— 43,400
Heat of combustion of gaseous hydrocyanic acid . . . . .	+ 166,000
Heat of combustion of gaseous cyanogen . . . . .	+ 172,000

Hydrocyanic acid, like other bodies whose formation from their elements is attended with absorption of heat—acetylene, for example—is very much inclined to condensation and polymerisation.

From an examination of the other methods of forming this compound, Berthelot infers that if it could be produced by directly combining cyanogen and hydrogen, each equivalent would absorb —4,800 heat-units. This reaction, as shown by Gay-Lussac, and confirmed by Berthelot, does not take place. Assuming this number from *a priori* considerations, it may be compared with the heat of formation of the analogous compounds of chlorine, bromine, and iodine:

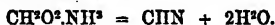
	Heat-units
ClH . . . . .	+ 23,900
BrH . . . . .	+ 12,300
IH . . . . .	+ 800
CyH . . . . .	— 2,400

The first three are formed directly, but with increasing difficulty as they descend in the series; the last cannot be formed directly.

Hydrocyanic acid is, however, formed directly, with absorption of heat, from acetylene and nitrogen, under the influence of the electric spark:



The production of hydrocyanic acid (formonitril) from ammonium formate throws some light on the theory of the amides:



This equation represents the full dehydration of ammonium formate. If it took place at ordinary temperatures with the solid salt, and with production of water and liquid hydrocyanic acid, there would be an absorption equal to —13,400 heat-units; if the salt were dissolved, and the products were water and gaseous hydrocyanic acid, the absorption would be about —38,000 units. But the dehydration might be accomplished in two steps, formamide and water being first produced:



and the formamide being then converted, by further loss of H<sup>2</sup>O, into formonitril or hydrocyanic acid; and in the two phases of this dehydration equal quantities of heat should be absorbed. This, however, would be true for gaseous products only. The combination of the elements of water with the amide to form the ammonia salt disengages 1,400 heat-units; with the nitril, 10,800.

*Potassium Cyanide*.—Experiment gives the following data:—

Hydrocyanic acid, in dissolving in 40 times its weight of water, emits heat equal to 400 heat-units. Dilute hydrocyanic acid and dilute potash give +2,800 units.







## II. Reciprocal Transformations of the Nitrogen Oxides.

		Heat-units
Monoxide	$\text{N}^2\text{O} = \text{N}^2 + \text{O}$	+ 18,000 (heat or electric spark).
	$2\text{N}^2\text{O} = \text{N}^2 + \text{N}^2\text{O}^2$	- 51,800 (imaginary reaction).
	$4\text{N}^2\text{O} = 3\text{N}^2 + \text{N}^2\text{O}^4$	+ 11,400 (spark).
Dioxide	$\text{N}^2\text{O}^2 = \text{N}^2 + \text{O}^2$	+ 88,800; then + $\text{N}^2\text{O}^2 = \text{N}^2\text{O}^4$ , or
	$2\text{N}^2\text{O}^2 = \text{N}^2 + \text{N}^2\text{O}^4$	125,000 (heat or spark).
	$\text{N}^2\text{O}^2 = \text{N}^2\text{O} + \text{O}^2$	68,800; then + $\text{N}^2\text{O}^2 = \text{N}^2\text{O}^3$ , or
	$2\text{N}^2\text{O}^2 = \text{N}^2\text{O} + \text{N}^2\text{O}^3$	91,000 (heat or spark).
Trioxide	$\text{N}^2\text{O}^3 = \text{N}^2\text{O}^2 + \text{O}$	- 22,000; then + $\text{N}^2\text{O}^3 = \text{N}^2\text{O}^4$ , or
	$2\text{N}^2\text{O}^3 = \text{N}^2\text{O}^2 + \text{N}^2\text{O}^4$	- 5,800

The trioxide dissolves in water without appreciable decomposition when the quantity of water is large and the temperature low; but with insufficient water or an elevated temperature, a double dissociation appears to take place, part of the hydrate being decomposed into water and anhydride, and a portion of the latter into dioxide and oxygen. The oxygen converts a further portion of nitrous acid into nitric acid, and the dioxide is evolved until, by the destruction of the nitrous acid, the solution has become so dilute that the tension of dissociation is balanced by the dioxide which remains dissolved.

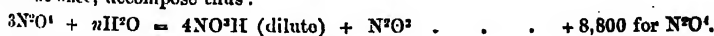
Tetroxide	$\text{N}^2\text{O}^4 = \text{N}^2 + \text{O}^4$	+ 48,600 (spark).
	$\text{N}^2\text{O}^4 = \text{N}^2\text{O}^3 + \text{O}$	- 16,200; then + $\text{N}^2\text{O}^4 = \text{N}^2\text{O}^5$ , or
	$2\text{N}^2\text{O}^4 = \text{N}^2\text{O}^3 + \text{N}^2\text{O}^5$ (gas)	- 12,800.

The last reaction is, however, imaginary. It is noticeable that the parallel reaction of the dioxide is real, and disengages heat; that of the trioxide, which absorbs a small amount of heat, leads to a dissociated system, and that of the tetroxide, which theoretically absorbs a larger quantity of heat, cannot be effected.

*Pentoxide.*— $\text{N}^2\text{O}^5$  (gas) =  $\text{N}^2\text{O}^4 + \text{O}$  . . . . . 3,400 heat-units.

The inverse reaction does not appear actually to take place. In the case where both  $\text{N}^2\text{O}^3$  and  $\text{N}^2\text{O}^4$  are liquid, this reaction would produce no thermic effect whatever.

The different modes of action between nitrogen tetroxide and water may be well illustrated by filling two tubes of different diameters with the vapours of the dry tetroxide, leaving rather more of the liquid in the narrow tube than in the wide one. After cooling, the tubes are opened under water, when the wide one fills entirely, owing to the reaction,  $\text{N}^2\text{O}^4 + n\text{H}^2\text{O} = \text{NO}^2\text{H}$  (dilute) +  $\text{NO}^2\text{H}$  (dilute) (which disengages 13,600 heat-units for  $\text{N}^2\text{O}^4 = 92$  grams). In the narrow tube, the vapours (and especially the liquid tetroxide), coming in contact with a smaller quantity of water at once, decompose thus:



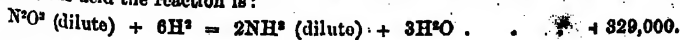
The tube remains partly filled with the dioxide.

## III. Action of Metals on Nitric and Nitrous Acids.

$\text{N}^2\text{O}^3\text{H}^2\text{O}$ (dilute)	= $\text{N}^2\text{O}^4$ (gas)	+ $\text{H}^2\text{O} + \text{O}$ (combined)	disengages	- 33,200 + Q*
"	= $\text{N}^2\text{O}^4$ (gas)	+ $\text{H}^2\text{O} + 2\text{O}$	"	- 49,400 + 2Q
"	= $\text{N}^2\text{O}^3$ (dissolved)	+ $\text{H}^2\text{O} + 2\text{O}$	"	- 36,400 + 2Q
"	= $\text{N}^2\text{O}^3$	+ $\text{H}^2\text{O} + 3\text{O}$	"	- 71,400 + 3Q
"	= $\text{N}^2\text{O}$	+ $\text{H}^2\text{O} + 4\text{O}$	"	+ 2,600 + 4Q
"	= $\text{N}^2$	+ $\text{H}^2\text{O} + 5\text{O}$	"	- 15,400 + 5Q
$\text{N}^2\text{O}^2$ dilute	= $\text{N}^2\text{O}^2 + \text{O}$ (combined)	disengages		- 35,000 + Q
"	= $\text{N}^2 + 3\text{O}$	"	"	- 51,800 + 3Q

The value -41,400 obtained by Favre for the reduction of  $\text{N}^2\text{O}^3$  to  $\text{N}^2\text{O}^2$  has been hitherto accepted. The presence of 9 p.c. of  $\text{N}^2\text{O}$  or 6 p.c. of free nitrogen in the gas evolved by the action of copper on nitric acid would account for the discrepancy.

IV. *Formation of Ammonia from Nitric Acid.*—If nitric acid be reduced to ammonia, by the nascent hydrogen evolved by a metal from dilute sulphuric or hydrochloric acid, the reaction  $\text{NO}^2\text{H}$  (dilute) +  $3\text{H} = \text{NH}^3$  (dilute) +  $3\text{H}^2\text{O}$  evolves + 21,500. With nitrous acid the reaction is:



Q is the quantity of heat produced by the union of 16 grams of oxygen with the metal employed.



The Heat-phenomena accompanying the transformation of Nitrogen Tetroxide into Nitric Acid, and the introduction of these two bodies into Organic Compounds have also been determined by Troost & Hautefeuille (*Compt. rend.* lxxiii. 378), with results agreeing nearly with those of Berthelot.—The heat evolved in the combination of 1 eq. liquid nitrogen tetroxide with oxygen gas to form nitric anhydride,  $N^2O^2$ , was found to be 23,500 units, the experiment being so made that the nitric anhydride was dissolved in 100 parts of water. The reduction of nitric anhydride by hydrogen, with formation of nitrogen tetroxide and water, yields therefore  $34,460 - 23,500 = 10,960$  units for 1 equivalent. The reduction of nitric acid to nitrogen tetroxide disengages more heat the greater the concentration; thus acid of the maximum density gives 17,500 heat-units; acid of sp. gr. 1.48 gives 17,100; acid of sp. gr. 1.46 gives 16,900; and acid of sp. gr. 1.43 gives 15,300.

The heat disengaged in the reduction of nitric acid (whatever be its state of concentration) in substitution is always much smaller than the total heat observed in the combustion of the substitution-compounds. The following table gives the principal results. The second column of figures shows the heat disengaged by the reduction of the nitric acid employed, as determined in each case:

Products of substitution	Heat disengaged by an equivalent of the organic body	Heat disengaged in the reduction of the nitric acid	Heat lost in the combination
Nitrobenzene . . .	38,400	16,900	21,500
Dinitrobenzene . . .	76,800	34,400	42,400
Nitrotoluene . . .	38,000	16,900	21,100
Dinitrotoluene . . .	76,000	34,400	41,600
Nitronaphthalene . . .	36,500	15,200	21,300
Dinitronaphthalene . . .	73,000	32,300	40,100

In the production of nitric ethers the amount of heat disengaged is not so great as with the substitution-compounds. This appears from the following table:—

Nitric ethers	Heat disengaged by an equivalent	Heat disengaged by an equivalent of the nitric acid used
Nitroglycerin . . . . .	19,000	6,330
Gun-cotton . . . . .	52,000	10,400
Nitromannite . . . . .	24,500	4,080

These results confirm Berthelot's conclusion, that, for a given quantity of nitrogen entering into combination, the available mechanical work is greater in the nitric ethers than in the nitro-substitution-products.

**Thermochemical Researches on the Ammonia Salts** (Berthelot, *Compt. rend.* lxxiii. 745, 864, 957, 1003, 1050).—These researches are divided into three parts, relating: 1. To the formation of ammonium salts of strong acids, such as hydrochloric, nitric, and sulphuric acid. 2. To that of the salts of weak acids, as carbonic, boric, hydrocyanic, phenic, and sulphydric acid. 3. To the reciprocal actions between various ammonium salts and the corresponding salts of the alkali-metals.

#### Part 1. Ammonium Salts formed by Strong Acids.

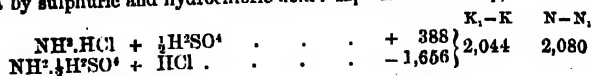
The following values relate to liquids containing  $\frac{1}{2}$  eq. in a litre, so that their mixture in equal volumes yields a liquid containing  $\frac{1}{2}$  eq. of neutral salt in the litre ( $1 : 210 H^2O$ ).

HCl + $NH^3$	12,630	12,270	mean	12,450	heat-units
$HNO^3$ + $NH^3$	12,630	12,620	"	12,570	"
$\frac{1}{2}H^2SO^4$ + $NH^3$	14,760	14,320	"	14,530	"

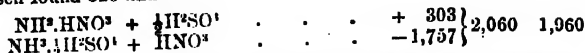
These numbers are not sensibly altered by the addition of an excess of water, or acid or ammonia.

These values were determined, in the first place, by the reciprocal action of acids and salts. The difference  $K_1 - K$  of the quantities of heat evolved in the two reactions (e.g. decomposition of ammonium chloride by sulphuric acid and of ammonium sul-

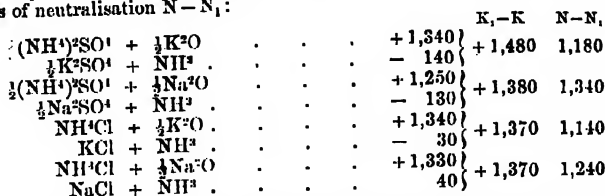
phate by hydrochloric acid) is equal to the difference of the heats of neutralisation of ammonia by sulphuric and hydrochloric acid:  $K_1 - K = N - N_1$ ;



Taomsen found 320 and 148.



Another mode of determination is found in the *reciprocal action of bases or salts*. The difference  $K_1 - K$  of the two quantities of heat thus evolved is likewise equal to the two heats of neutralisation  $N - N_1$ :



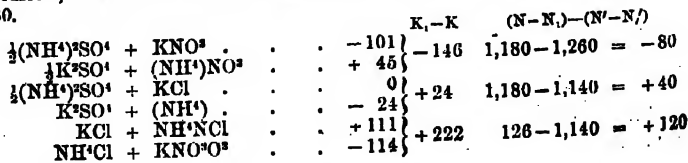
These calculations of  $N - N_1$  depend upon the knowledge of the developments of heat attending upon the action of other bases on the same acids.

	Berthelot	Thomsen
$\frac{1}{2}\text{H}_2\text{SO}_4 + \frac{1}{2}\text{K}_2\text{O}$	15,710	15,645
$\text{HCl} + \frac{1}{2}\text{K}_2\text{O}$	13,590	13,750
$\text{HNO}_3 + \frac{1}{2}\text{K}_2\text{O}$	13,830	13,770
$\frac{1}{2}\text{H}_2\text{SO}_4 + \frac{1}{2}\text{Na}_2\text{O}$	15,870	15,690
$\text{HCl} + \frac{1}{2}\text{Na}_2\text{O}$	13,690	13,740
$\text{HNO}_3 + \frac{1}{2}\text{Na}_2\text{O}$	13,720	13,680
$\frac{1}{2}\text{H}_2\text{SO}_4 + \frac{1}{2}\text{CaO}$	16,020	15,570
$\text{HCl} + \frac{1}{2}\text{CaO}$ (dissolved)	13,850	13,950
$\frac{1}{2}\text{H}_2\text{SO}_4 + \frac{1}{2}\text{BaO}$	18,400	18,450

A third mode of determination adopted by Berthelot consists in causing four salts, formed by two bases and two acids, to act on one another in pairs (*the reciprocal action of salts*). The difference of the two thermal effects  $K_1 - K$  is said to be equal to the excess obtained by subtracting the difference of the heat of neutralisation of the two acids by the one base from the same difference for the other base:

$$K_1 - K = (N - N_1) - (N' - N'_1)$$

But the examples adduced do not afford very satisfactory evidence in favour of this conclusion; it is difficult to see, for example, in what sense 146 can be said to be equal to 80.



## Part 2. Ammonium Salts formed by Weak Acids

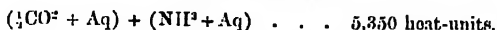
### Boric Acid.

	Heat-units
$\text{B}_2\text{O}_3$ (1 eq. cryst. acid, i.e. 70 grams of boric anhydride in 4 litres of liquid) + $\text{NH}_3$ (1 eq. in 2 litres)	8,980
+ $\text{NH}_3$ (second eq.)	2,620
+ $\text{NH}_3$ (third eq.)	1,050
	12,650
$\text{H}_3\text{BO}_3$ (samoliquid) + $\text{NH}_3$ (1 eq. in 4 lit.)	5,440
$\text{B}_2\text{O}_3 \cdot \frac{1}{2}(\text{NH}_4)_2\text{O}$ (1 eq. in 4 lit.) + 1 vol. water	2,800
+ 5 "	2,170

$\text{B}^2\text{O}^3$ (1 eq. in 4 lit.)	+ $\frac{1}{2}\text{Na}^2\text{O}$ (1 eq. in 2 lit.)	Heat-units	
	+ $\frac{1}{2}\text{Na}^2\text{O}$ (second eq.)	11,560	19,820
	+ $\frac{1}{2}\text{Na}^2\text{O}$ (third eq.)	8,260	
$\text{B}^2\text{O}^3$ (same liquid)	+ $\frac{1}{2}\text{Na}^2\text{O}$ (1 eq. in 4 lit.)	170	
$\text{B}^2\text{O}^3 \cdot \frac{1}{2}\text{Na}^2\text{O}$ (1 eq. in 4 lit.)	+ 1 vol. water	11,130	
	+ 5 "	560	
Dissodic Borate (the above liq.)	+ 5 "	780	
Trisodic Borate	+ 5 "	145	
		166	

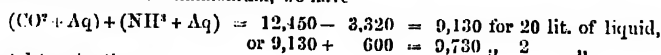
Here then there is a progressive decomposition of the ammonium borate by water, deeper and more rapid than that of the sodium borate.

#### Carbonic Acid.

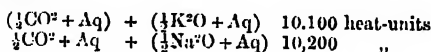


This value relates to a solution of 1.250 grm. carbonic anhydride in the litre or 1 eq. of salt produced in 20 litres.

Moreover, the solution of ammonium bicarbonate in 50 pts. water gave -6,280 heat-units for 1 eq. A solution of 79 gms. in 2 litres gave, on dilution with 9 vol. water -600 heat-units for 1 eq. The decomposition of this salt (1 eq. in 20 lit.) by hydrochloric acid gave 3,320 units; and since dissolved carbonic acid has no appreciable action on a solution of sal-ammonium, we have



Indirect determinations:—

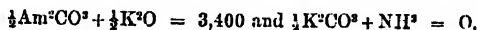


For the formation of the bicarbonates of sodium and potassium Berthelot assumes the values 1,110 and 1,100; greater dilution produced scarcely any alteration in the amount of heat evolved.

#### (1.) Neutral Carbonate, $\frac{\text{Am}^2\text{CO}^3}{2}$ .

$\frac{1}{2}\text{Am}^2\text{CO}^3$ (1 eq. in 4 lit.)	+ $\text{KNO}^3$ (1 eq. in 4 lit.)	- 120	K, -K N (calc.)	
$\frac{1}{2}\text{K}^2\text{CO}^3$ "	+ $\text{AmNO}^3$ "	- 3,220		+ 3,110 5,730
$\frac{1}{2}\text{Am}^2\text{CO}^3$ "	+ $\text{NaCl}$ "	- 20		+ 3,040 6,000
$\frac{1}{2}\text{Na}^2\text{CO}^3$ "	+ $\text{AmCl}$ "	- 3,060		
$\frac{1}{2}\text{Am}^2\text{CO}^3$ "	+ $\frac{1}{2}\text{K}^2\text{SO}^4$ "	- 100		+ 3,080 5,830
$\frac{1}{2}\text{K}^2\text{CO}^3$ "	+ $\frac{1}{2}\text{Am}^2\text{SO}^4$ "	- 3,180		

These values agree nearly enough with the above value, 7,170, for liquid of half this degree of dilution. They were obtained at 22°. N appears to increase slightly with decreasing temperature. The value 6,700 was actually found by the combination of—



#### (2.) Ammonium Bicarbonate, $\text{AmHCO}^3$ .

$\text{AmHCO}^3$ (1 eq. in 4 lit.)	+ $\text{KNO}^3$ (1 eq. in 4 lit.)	- 40	K, -K N (calc.)	
$\text{KHCO}^3$ "	+ $\text{AmNO}^3$ "	- 80		+ 40 0,720
$\text{AmHCO}^3$ "	+ $\text{NaCl}$ "	0		+ 260 9,620
$\text{NaHCO}^3$ "	+ $\text{AmCl}$ "	- 260		
$\text{AmHCO}^3$ "	+ $\frac{1}{2}\text{K}^2\text{SO}^4$ "	+ 20		+ 140 9,700
$\text{KHCO}^3$ "	+ $\frac{1}{2}\text{Am}^2\text{SO}^4$ "	- 120		
$\text{AmHCO}^3$ "	+ $\frac{1}{2}\text{K}^2\text{O}$ "	+ 4,940		+ 1,170 9,836
$\text{KHCO}^3$ "	+ $\text{NH}^3$ "	+ 3,770		

These values agree with that previously found, namely 9,730.

Dissolved carbonic acid evolved no sensible heat in its action on solutions of ammonium bicarbonate. In presence of water, on the other hand, the action of ammonia on carbonic acid increases with its quantity, as in the case of boric acid and of phenol. The heat evolved in the action of 1 eq. carbonic acid on varying quantities of ammonia varied from 5,300 to 7,400 units, becoming greater as the concentration increased.

The neutral carbonates of potassium and sodium may be mixed together or with other neutral fixed alkali-salts without perceptible evolution or absorption of heat. The bicarbonates of potassium and sodium exhibit the same behaviour. So likewise

does ammonium bicarbonate; it is but slightly decomposable by water or by stable neutral salts, as potassium nitrate, sodium sulphate, sodium chloride, or ammonium chloride; neither does it act on bicarbonate of potassium.

With neutral ammonium carbonate the case is different:

					Heat-units
$\frac{\text{Am}^2\text{CO}^3}{2}$	(1 eq. in 4. lit.)	+	$\frac{\text{K}^2\text{CO}^3}{2}$	(1 eq. in 2 lit.)	- 360
"	"	+	1	"	- 1,290
"	"	+	1 $\frac{1}{2}$	"	- 1,540
"	"	+	2	"	- 1,660
$\text{KHCO}^3$	(1 eq. in 4 lit.)	+	$\frac{\text{Am}^2\text{CO}^3}{2}$	(1 eq. in 2 lit.)	+ 560
"	"	+	1	"	+ 800
"	"	+	1 $\frac{1}{2}$	"	+ 980
"	"	+	2	"	+ 1,106

On the other hand, ammonium bicarbonate is decomposed by potassium carbonate and sodium carbonate with absorption of heat:

$\text{KHCO}^3$	(1 eq. in 4 lit.)	+	$\frac{1}{2} \text{K}^2\text{CO}^3$	(1 eq. in 2 lit.)	- 940
"	"	+	1	"	- 1,170
"	"	+	1 $\frac{1}{2}$	"	- 2,290
"	"	+	2	"	- 2,690

Ammonium bicarbonate is attacked even by the neutral carbonate—

$\text{AmH}$	(1 eq. in 2 lit.)	+	$\frac{1}{2} \text{Am}^2\text{CO}^3$	(1 eq. in 2 lit.)	+ 620
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a result which would be inexplicable if the two carbonates could really mix without alteration.

Lastly, the solution of potassium carbonate is not attacked by ammonia, whilst the solution of neutral ammonium carbonate progressively absorbs heat as ammonia is gradually added to it.

From the preceding observations Berthelot infers that weak acids are characterised by imperfect combination, and by a division of the base of a salt between the acid and the water. The vague notions hitherto entertained respecting the distinction between strong and weak acids and bases may thus be reduced to greater precision. A *strong acid* and a *strong base*, form, by their union, neutral stable salts which are not perceptibly decomposed by water, and are not modified by excess of base; to this class of salts belong the sulphates, chlorides, and nitrates of potassium and sodium. On the other hand, a *weak acid* forms with all strong bases, and especially with ammonia, neutral salts which are partially decomposed by water. Moreover, the energy of weak acids exhibits different degrees, recognisable by the heat-phenomena produced by the action of water on their salts, and by the progressive action of several equivalents of ammonia. These differences of energy are strikingly displayed in the following double decompositions of salts:—

### Part 3. Reciprocal Action of the Ammonia Salts and the Salts of the Fixed Alkalis.

1. *Both Salts formed by Strong Acids* (1 equivalent of each salt previously dissolved in such a manner that the volume of the liquid shall be 2 litres):

$\frac{1}{2} \text{Am}^2\text{SO}^4$	+	$\text{KNO}^3$	.	.	.	.	.	- 100
$\frac{1}{2} \text{K}^2\text{SO}^4$	+	$\text{AmNO}^3$	.	.	.	.	.	40
$\frac{1}{2} \text{Am}^2\text{SO}^4$	+	$\text{KCl}$	.	.	.	.	.	0
$\frac{1}{2} \text{K}^2\text{SO}^4$	+	$\text{AmCl}$	.	.	.	.	.	- 20
$\frac{1}{2} \text{AmNO}^3$	+	$\text{KCl}$	.	.	.	.	.	+ 110
$\frac{1}{2} \text{KNO}^3$	+	$\text{AmCl}$	.	.	.	.	.	- 110
$\text{C}^2\text{H}^3\text{AmO}^2$	+	$\text{NaCl}$	.	.	.	.	.	+ 120
$\text{C}^2\text{H}^3\text{NaO}^2$	+	$\text{AmCl}$	.	.	.	.	.	- 20

The heat-phenomena developed on diluting the same saline solutions with an equal volume of water at the same temperature are as follow:—

$\frac{1}{2} \text{K}^2\text{SO}^4 + \text{Aq}$	- 70	$\frac{1}{2} \text{Na}^2\text{SO}^4 + \text{Aq}$	- 70	$\frac{1}{2} \text{Am}^2\text{SO}^4 + \text{Aq}$	+ 20
$\text{KCl} + \text{Aq}$	+ 90	$\text{NaCl} + \text{Aq}$	- 20	$\text{AmCl} + \text{Aq}$	+ 10
$\text{KNO}^3 + \text{Aq}$	- 160	$\text{NaNO}^3 + \text{Aq}$	- 110	$\text{AmNO}^3 + \text{Aq}$	- 100

From this it appears that the mixing of two neutral stable salts is always attended with slight evolution or absorption of heat, which, however, is not the case of the

actions of water on the two solutions in the separate state. Hence Berthelot concludes that the thermoneutrality of salts asserted by Hesso (*Ann. Chim. Phys.* 1842 [3], iv. 222) does not exist. The true law of the mutual action of salts is represented, according to Berthelot, by the equation (p. 628):

$$K_1 - K = (N - N_1) - (N' - N'_1).$$

2. One Salt formed by a Strong, the other by a Weak Acid.

a. Neutral Carbonates.

	Heat-units
$\frac{1}{2}K^2CO^3 + AmNO^3$	-3,220
$\frac{1}{2}Am^2CO^3 + KNO^3$	-120
$\frac{1}{2}K^2CO^3 + \frac{1}{2}Am^2SO^4$	-3,180
$\frac{1}{2}Am^2CO^3 + \frac{1}{2}K^2SO^4$	-100
$\frac{1}{2}Na^2CO^3 + AmCl$	-3,060
$\frac{1}{2}Am^2CO^3 + NaCl$	-20

These numbers show that stable ammonia salts, in presence of water, are almost completely decomposed by the carbonates of potassium and sodium, with formation of the still more stable nitrates, chlorides, and sulphates of the potassium and sodium, and of the least stable carbonate of ammonium. The latter being immediately decomposed in presence of water gives rise to the observed thermic effect, corresponding with a complete or at least a considerable action.

b. The bicarbonates of potassium, sodium, and ammonium, being stable in water, exhibit but feeble thermal effects in their reaction with neutral stable alkali-salts, inasmuch as the latter also do not give rise to any salt decomposable by water with absorption of heat.

c. Phenates (1 eq. in 11.5 litres).

$C^6H^5NaO + AmCl$	-4,100 heat-units
$C^6H^5AmO + NaCl$	+100 "
$C^6H^5NaO + \frac{1}{2}Am^2SO^4$	-4,300 "

Hence it appears that sodium phenate in presence of stable ammonia salts is completely or almost completely decomposed into sodium chloride, sulphate, &c., and ammonium phenate.

d. Borates (1 eq. in 11.5 litres).

$\frac{Na^2O}{2} B^2O^3 + AmCl$	-2,250	$\frac{Na^2O}{2} B^2O^3 + \frac{1}{2}Am^2SO^4$	-2,250
$\frac{Am^2O}{2} B^2O^3 + NaCl$	-480	$\frac{Am^2O}{2} B^2O^3 + \frac{1}{2}Na^2SO^4$	-460

The chief product of these reactions is ammonium borate. The borates of sodium and ammonium appear, however, to act upon one another:

$$\frac{Na^2O}{2} B^2O^3 + \frac{Am^2O}{2} B^2O^3 \quad . \quad . \quad . \quad -200;$$

while, on dilution with an equal volume of water, sodium borate alone gives -560, and ammonium borate -1,000 heat-units.

e. Cyanides.

$KCy$ (1 eq. in 2 litres) + $AmCl$ (1 eq. in 2 litres)	-600
$AmCy$ + $KCl$	-40
$KCy + \frac{1}{2}Am^2SO^4$	-590

The entire transformation of potassium cyanide into ammonium cyanide and potassium chloride (or sulphate) would give  $1,140 - (2,940 - 1,300) = -500$  heat-units, to which, on account of the dilution, must be added -100, giving the number -600, obtained as above.

According to Thomsen, whose results are confirmed by Berthelot, the sulphides of potassium, sodium, and ammonium, are completely resolved by water into sulphhydrate and free alkali. But the sulphhydrates are stable in presence of water, or if not completely, at least as much so as the bicarbonates:



This quantity of heat answers to the action of 1 eq. free soda on ammonium chloride, both of which come into play in the reaction.





From this number he calculates the heat of combustion of formic acid, as well as the heat evolved in the formation of the acid from its elements:—

Heat-units		Heat-units
147 =	$(\text{CO}^2\text{H}^2, \text{Aq})$	
13,200 =	$(\text{CO}^2\text{HKAq}, \text{KAq})$	$\{(\text{CO}^2\text{H}^2, \text{O}) = 60,193$
72,912 =	$(\text{CO}^2\text{HKAq}, \text{O}, \text{KAq})$	$\{(\text{CO}^2, 2\text{KAq}) = 26,066$
86,259		89,259

This calculation gives 60,193 heat-units for the heat developed by the complete oxidation of a molecule of formic acid to water and carbon dioxide, which is about 36,000 less than the amount determined by Favre & Silbermann, and adopted by Berthelot.

In the formation of formic acid from its elements, the development of heat is calculated to amount to 105,124 heat-units:—

$(\text{C}, \text{H}^2, \text{O}^2) + (\text{CH}^2\text{O}^2, \text{O}) = (\text{C}, \text{O}^2) + (\text{H}^2, \text{O})$	
105,124 + 60,193 = 96,960 + 68,375	
Heat-units	Heat-units

Thomsen further shows that the formation of the acid from carbon monoxide and water would be accompanied by an evolution of 6,607 heat-units; that the formation of sodium formate from carbon monoxide and sodium hydrate is attended with a development of at least 19,954 heat-units; that the formation of the acid from carbon dioxide and hydrogen would likewise be attended with an evolution of heat amounting to 8,164 heat-units; that the heat absorbed in the decomposition of formic acid into carbon monoxide and water by sulphuric acid is compensated by the heat evolved in the union of the sulphuric acid with the water; and that the decomposition at a high temperature of the vapour of formic acid into carbon dioxide and hydrogen, and the rise of temperature which Berthelot has observed to accompany that decomposition, are perfectly normal phenomena. He therefore concludes that formic acid does not present the remarkable anomalies in the heat-phenomena of its formation and decomposition, which Berthelot supposes it to exhibit (*Deut. Chem. Ges. Ber.* v. 957). See further, Berthelot (*Compt. rend.* lxxvi. 1433; *Chem. Soc. J.* 1874, 1099).

**Heat evolved in the Combination of Sulphuric Acid and Water.**—The quantities of heat evolved in the hydration of sulphuric acid have been determined by different observers, not always with concordant results. The following table exhibits these determinations of the quantities of heat in kilogram-degrees evolved by the mixture of 1 mol. hydrogen sulphate,  $\text{H}^2\text{SO}^4$ , with 1, 2, 3 . . . mol. water; the numbers being reduced, when necessary, to a common unit:—

1 gram $\text{H}^2\text{SO}^4$	Abria	Hess	Hess	Favre & Silbermann	Thomsen	Favre & Quillard
$\text{H}^2\text{SO}^4$ with $\text{H}^2\text{O}$ . .	64.2	63.5	77.7	64.7	65.3	66.4
" 2 $\text{H}^2\text{O}$ . .	94.7	95.3	110.4	94.6	—	99.5
" 3 $\text{H}^2\text{O}$ . .	113.0	—	—	111.9	111.9	118.3
" 4 $\text{H}^2\text{O}$ . .	124.2	—	—	122.2	—	130.1
" 5 $\text{H}^2\text{O}$ . .	131.1	127.1	148.9	130.7	130.3	139.2
" 6 $\text{H}^2\text{O}$ . .	—	—	—	136.2	—	146.9
" 7 $\text{H}^2\text{O}$ . .	—	—	—	141.8	—	152.9
" 8 $\text{H}^2\text{O}$ . .	—	—	—	145.1	—	—
" 9 $\text{H}^2\text{O}$ . .	—	—	—	148.5	—	—
" excess of water . .	—	—	—	148.5	17.6	—

Pfaundler (*Jahresb. f. Chem.* 1869, 122) has measured the quantities of heat evolved by the different hydrates of sulphuric acid when mixed with an excess of water, and has thence calculated the values sought. The hydrate to be examined was enclosed in quantities between 10 and 50 grams in thin narrow-necked glass bulbs, which were weighed before and after filling. One of these bulbs was placed in a small shallow basket suspended in the calorimeter, and moved about in the water—the quantity of which was calculated so as to yield, on mixing, the hydrate  $\text{SO}^2 \cdot 120\text{H}^2\text{O}$  or  $\text{H}^2\text{SO}^4 \cdot 119\text{H}^2\text{O}$ —till the water and acid had attained the same temperature. The thermometer was then read off, and the bulb immediately broken. The acid, on stirring, mixed with the entire liquid in less than a second, and the thermometer rose quickly and soon came to rest, the large quantities of liquid employed and the short duration of the experiment rendering the influence of the surrounding strata of air quite im-

perceptible. From the observed results, the values in the following table were determined:—

Formula	Quantity of heat evolved with an excess of water		Quantities of heat evolved in the formation of several hydrates from 1 gram of monohydrate, $\text{H}^2\text{SO}^4$	Quantities of heat evolved on addition of each molecule of water to 1 gram of monohydrate
	Per gram of substance	Per gram of monohydrate, $\text{H}^2\text{SO}^4$ , contained in the substance		
$\text{SO}^3 \cdot \text{H}^2\text{O}$	181.16	181.16	0	0
$\text{SO}^3 \cdot 2\text{H}^2\text{O}$	130.66	142.69	38.47	—
$\text{SO}^3 \cdot 3\text{H}^2\text{O}$	94.15	111.44	69.72	69.72
$\text{SO}^3 \cdot 4\text{H}^2\text{O}$	73.06	93.10	87.97	—
$\text{SO}^3 \cdot 5\text{H}^2\text{O}$	56.84	77.72	103.44	33.72
$\text{SO}^3 \cdot 6\text{H}^2\text{O}$	47.05	68.66	112.50	—
$\text{SO}^3 \cdot 7\text{H}^2\text{O}$	40.15	62.31	118.85	15.41
$\text{SO}^3 \cdot 8\text{H}^2\text{O}$	28.50	49.43	131.73	12.88
$\text{SO}^3 \cdot 9\text{H}^2\text{O}$	21.04	40.36	140.80	9.07
$\text{SO}^3 \cdot 10\text{H}^2\text{O}$	15.73	33.07	148.09	7.27
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$\text{SO}^3 \cdot 120\text{H}^2\text{O}$	0	0	181.16	—

The numbers in the last column but one are immediately comparable with those of former observers given in the preceding table. Some of them agree most nearly with those of Favre & Silbermann, others with those of Favre & Quillard.

**Heat disengaged in the Reaction between the Haloid Acids and Water, and its relation to the Molecular Volume of the Solutions** (Berthelot, *Compt. rend.* lxxvi. 679).

1. *Hydrochloric Acid*.—A molecule of the gas, (36.5 grams) in presence of 100 to 400 times its weight of water disengages 17,480 heat-units (gram-degrees), and when aqueous hydrochloric acid of different degrees of concentration is diluted with water, the heat disengaged varies inversely as the quantity of water already united with the hydracid. The molecular volume of the solution  $\text{HCl} + n\text{H}^2\text{O}$  is expressed by the formula:

$$V = 18n + \frac{10}{n}.$$

2. *Hydrobromic Acid*.—The heat evolved in this case by a molecule of the gas is 20,700 heat-units, and the effects of dilution are the same as those produced with hydrochloric acid, except that, at the maximum of concentration, the solutions of hydrobromic acid disengage somewhat more heat, a relation analogous to that obtained with the two gases. The molecular volume of the solution  $\text{HBr} + n\text{H}^2\text{O}$  is expressed nearly by the formula:

$$V = 18n + 25.5 + \frac{7}{n}.$$

3. *Hydriodic Acid*.— $\text{HI} + 700 \text{H}^2\text{O}$  disengages 19,570 heat-units, and the heat disengaged on diluting the concentrated solution is nearly the same as that from hydrochloric acid and hydrobromic acid, from which it would appear that the molecular work accomplished in the reaction by these three hydracids on the same number of equivalents of water is the same. The formula representing the molecular volume of the solution  $\text{HI} + n\text{H}^2\text{O}$  is

$$V = 18n + 35.5.$$

At  $0^\circ \text{C}$ . one volume of water dissolves 500 volumes of hydrochloric acid gas, and at  $-12^\circ$ , 560 volumes; of hydrobromic acid at  $10^\circ$ , about 600 volumes; and of hydriodic acid about 425 volumes.

An almost constant difference is observed between the molecular volumes of dilute solutions of hydriodic acid and hydrochloric acid, and also between hydrobromic acid and hydrochloric acid, which in the former case is 17.3 c.c., and in the latter 23.4 c.c. The same differences are found in dilute solutions of the chlorides, bromides, and iodides of potassium, sodium, and ammonium; also between the solid salts the volume occupied by KI being 17.2 c.c. greater than that of KCl, and  $\text{KBr}$  7.3 c.c. greater than KCl. Nearly the same differences in the molecular volumes exist in certain organic compounds, such as the chloride and iodide of acetyl. In numerous cases, however, this does not obtain, as in the comparison of the metallic salts, where the same is found

that the molecular volume of a chloride is less than that of the bromide, and this again less than the corresponding iodide. This agrees with the thermic results obtained in the formation of these compounds, the formation of chlorides disengaging more heat than that of the bromides, which in their turn disengage more than the corresponding iodides. It would seem, moreover, that the formation of compounds which present an almost constant difference between their molecular volumes, corresponds with a nearly constant difference in the amount of heat disengaged.

**Thermal Phenomena of Double Decomposition.**—*a.* Bertholot and Longuine (*Compt. rend.* lxi. 626) have examined the thermal effects produced in double decompositions which are completed in a short time and at ordinary temperatures, without yielding secondary products. Such reactions are found in the decomposition of the chlorides and anhydrides of acid radicles by water and alkalis. The acid chloride, or dilute acid solution, was introduced into a weighed quantity of water or dilute alkali, contained in a platinum calorimeter, its quantity determined by a final weighing, and verified by alkalimetric determinations. The correction for cooling was always less than  $\frac{1}{100}$ , and sometimes as little as  $\frac{1}{1000}$  of the entire rise of temperature.

**Decomposition of Acetyl Chloride by Water.**—For 1 eq. = 78.5 grams of acetyl chloride, the mean of three determinations gave 23,300 heat-units. The heat of solution of 1 eq. hydrochloric acid gas is, according to the mean of four experiments, 17,430 heat-units, and that of 1 eq. fused glacial acetic acid about 400 heat-units. Consequently, the heat evolved in the reaction  $C^2H^3OCl + H^2O = C^2H^3O^2 + HCl$  is  $23,300 - 17,400 - 400 = 5,500$  units, if the several bodies are supposed to be in their ordinary state.

The heat of combination of 1 eq. hydrochloric acid with 1 eq. potash in dilute solutions was found, as the mean of two experiments, in accordance with Favre & Silbermann's determination, to be 15,700 units, which number, taking account of the specific heat of solutions of calcium chloride (p. 600), must be reduced to 14,900. The heat of combination of 1 eq. acetic acid with potash amounted, in the mean of three experiments, to 14,100 units, which, taking account of the specific heat of solutions of potassium acetate, will be reduced to about 13,400.

**Decomposition of Acetyl Bromide by Water.**—The mean of three determinations gave, for 1 eq. = 123.0 heat-units, the heat of solution of 1 eq. hydrobromic acid gas was found, as the mean of four experiments, to be 21,150. Hence the heat evolved in the reaction  $C^2H^3OB^r + H^2O = C^2H^3O^2 + HBr$  is  $23,300 - 21,150 - 400 = 1,750$  units, the several bodies being supposed to be in their ordinary state.

**Decomposition of Acetyl Iodide by Water.**—Three determinations gave, as a mean for 1 eq., 21,400 heat-units. The heat of solution of 1 eq. hydriodic acid was found, as a mean of three experiments, to be 19,570 units. Hence the heat evolved in the reaction  $C^2H^3OI + H^2O = C^2H^3O^2 + HI$  is  $21,400 - 19,570 - 400 = 1,830$  units.

**Decomposition of Butyryl Bromide by Water.**—The heat evolved for 1 eq. was 27,000 units. But the experiment lasted nearly an hour, and correction for cooling amounted to nearly  $\frac{1}{10}$ th of the total value. The result was therefore checked by the decomposition with dilute potash, which gave 56,100 heat-units. If, from this, we deduct the heat of combination of butyric acid with potash in dilute solutions, which appears, from the mean of two experiments, to be 14,950 units, also the heat of combination of dilute hydrobromic acid with potash, which, according to Favre, is 15,500 units, we find indirectly, for the heat of decomposition of butyryl bromide by water, 25,650 units. The mean of the direct and indirect values is 26,300 units. The heat of solution of 1 eq. butyric acid in water was found to be about 600 units. Hence the heat evolved in the reaction  $C^4H^7OBr + H^2O = C^4H^7O^2 + HBr$  is  $26,300 - 21,150 - 600 = 4,550$  units, the several bodies being supposed to be in their ordinary state.

**Decomposition of Acetic Anhydride by Water.**—For 1 eq. = 102 grams the mean of two experiments gave 12,800 heat-units. The duration of the experiment for an hour rendered necessary a correction for cooling amounting to  $\frac{1}{10}$ th of the total value. After deduction of heat of solution of acetic acid, the reaction  $(C^2H^3O)^2O + H^2O = 2C^2H^3O^2$  gave 12,000 heat-units.

***β.* Thermal Effects accompanying the Dilution of Solutions, and Influence of Water in Double Decompositions.**—Marignac (*N. Arch. Ph. Nat.* xxxvi. 310; *Compt. rend.* lxi. 1180) has examined these phenomena by means of solutions containing 1 gram of substance in the anhydrous state, or (in the case of acids and salts) containing only constitutional water, in 10, 20, 40 . . . c.c.; such solutions are designated as  $\frac{1}{10}$ ,  $\frac{1}{20}$ ,  $\frac{1}{40}$  . . . solutions. The thermic effect of dilution was determined by mixing each solution with an equal volume of water. The total quantity of the mixed liquid usually amounted to 500–600 c.c. The thermometers used indicated the temperature to  $\frac{1}{500}$ th of a degree. The results are as follow:—

1. The addition of water to the solution of a single body produces a positive or negative alteration (rise or fall) of temperature, which, for the most part, does not exceed  $0.2^{\circ}$  for  $\frac{1}{10}$ -solutions, diminishes to  $\frac{1}{2}$  for dilution to  $\frac{1}{20}$ , and to  $\frac{1}{8}$  for dilution to  $\frac{1}{80}$ ; and may therefore be neglected below this limit. This rule, however, does not apply to all cases. Thus, in the dilution of sulphuric acid, the rise of temperature increases the more the solutions are diluted, amounting to 92, 135, 185, and 255 heat-units for 1 eq. (= 49), accordingly as the solutions were diluted to  $\frac{1}{10}$ ,  $\frac{1}{20}$ ,  $\frac{1}{40}$ , or  $\frac{1}{80}$ .

2. The mixture of the solutions of two salts which do not act on one another, produces in general less alteration of temperature than the simple dilution of these solutions. Development of heat takes place most frequently in cases where the two salts may be supposed not to act on one another, e.g. with two salts of the same base, and absorption of heat when they are capable of forming a double salt. Sometimes, however, the thermic action in these reactions is much more considerable, as in the mixing of sulphates of alkali-metal with sulphuric acid, which is attended with considerable absorption of heat.

3. The dilution of a solution containing two salts which do not act on one another with an equal volume of water, generally produces a very slight thermal effect, which is nearly equal to the sum of the thermal effects produced by diluting the two salts separately, and decreases rapidly as the solutions are more diluted. A remarkable exception to this rule is exhibited by the dilution of the acid sulphates of the alkali-metals, which is attended with a considerable absorption of heat, rapidly increasing with the dilution. In the case of acid sodium sulphate this thermal effect increases for 1 eq. from 58 heat-units for a  $\frac{1}{10}$ -solution to 525 units for a  $\frac{1}{80}$ -solution. This result affords the explanation and, to a certain extent, the measure of the decomposition of this salt by water.

4. The mixing of two saline solutions, or of a salt and an acid which decompose one another without forming an insoluble product, gives rise to more or less considerable thermal effects, which Marignac has not yet completely studied on account of the difficulty of separating them from the complicated effects resulting from the dilution of the solutions employed. The experiments have therefore been limited to a small number of bodies, merely to ascertain how the results vary according to the degree of dilution. These preliminary experiments show that the thermal effect varies considerably with the degree of dilution, and therefore that the chemical action may also vary therewith. Thus the action of sulphuric acid on a mixture of 55 quantity of sodium sulphate evolves 218 units of heat for  $\frac{1}{10}$ -, and 539 units for  $\frac{1}{80}$ -solutions. On the other hand, in the action of nitric acid on sodium sulphate, there is an absorption of heat varying from 1,965 to 1,255 units, accordingly as  $\frac{1}{10}$ - or  $\frac{1}{80}$ -solutions are employed. That different chemical actions really take place in these cases follows also from the thermal effect produced on diluting such a mixture. Equivalent quantities of sulphuric acid and sodium nitrate, mixed in  $\frac{1}{10}$ -solutions, yield -90, +45, +169, and +388 heat-units, when diluted to  $\frac{1}{20}$ ,  $\frac{1}{40}$ ,  $\frac{1}{60}$ , and  $\frac{1}{80}$ . Similar effects may also take place on mixing the solutions of two neutral salts. The mixing of equivalent quantities of aluminium sulphate and sodium acetate is attended by an absorption of heat varying from 2,454 to 3,047 units for a dilution of  $\frac{1}{10}$  to  $\frac{1}{80}$ . This experiment shows further the incorrectness of the assumed principle of *thermo-neutrality*, according to which double decomposition between two neutral salts should not be accompanied by any change of temperature. Moreover, it does not appear to be a matter of indifference whether two concentrated salt-solutions are first mixed and then diluted, or first diluted and then mixed. Dilution after the mixing of concentrated solutions does not appear to bring about so complete a state of equilibrium, or to produce this effect so quickly, as the mixing of previously diluted solutions.

**Decomposition by Heat. Dissociation—Thermolysis** (F. Mohr, *Ann. Ch. Pharm.* clxxi. 361).

The term 'dissociation' was originally applied by Deville to signify the separation of a compound into its elements, ultimate or proximate, by the agency of heat alone without the intervention of any other substance capable of breaking up the combination by its superior affinity for one of the elements. It has sometimes been used to denote more especially those decompositions by heat in which only a partial separation of the constituents take place; but the original signification is the most convenient and is most generally adopted. As however, 'Dissociation' might be applied equally well to the separation of a mass into its constituent particles, similar or dissimilar, by mechanical or any other means, Mohr proposes to replace it by the more specific term 'Thermolysis.'

An essential condition of decomposition by heat is that one or both the constituent elements be capable of assuming the gaseous state: compounds like borates and silicates, both whose constituents are fixed in the fire, are never decomposed by heat alone.

Another essential condition of thermolysis is that the constituents of the compound shall, in combining, have given out heat; and the process of thermolysis consists in restoring to the elements the heat which they have lost in combination. When 1 gram of hydrogen gas unites with 8 grams of oxygen to form water, a quantity of heat is evolved capable of raising the temperature of 34,462 grams of water by  $1^{\circ}$  centigrade, the two gases and the water produced being supposed to be at the temperature of  $0^{\circ}$  C. Whence is this heat derived? It did not pre-exist in the gases as heat, at least not as sensible or communicable heat; but the gases in combining have lost that peculiar movement of their atoms and molecules, which is the essential condition of the gaseous state, and have been converted into the much less volatile compound, water. Now it is just this quantity of motion which, in the act of combination, is converted into sensible heat, amounting to 34,462 units; and if the water is to be resolved into its constituents, these 34,462 units of heat must be restored to the elements, and reconverted into the kind of motion which is essential to the gaseous state. This may be effected in two ways:—

1. *By Thermolysis*, whereby the heat is restored to the water directly, either by means of Grove's white-hot platinum ball, or Deville's white-hot platinum tube (1st Suppl. 426).

2. *By Electrolysis*. In this mode of decomposition the required quantity of motion is imparted to the elements of water in the form of an electric current, which may be generated by dissolving zinc in acidulated water. Now a given quantity of oxygen develops more heat in combining with zinc than in combining with an equivalent quantity of hydrogen: hence when the zinc decomposes water, with formation of zinc-oxide and liberation of hydrogen, there is an excess of heat available for conversion into other forms of energy; and this excess, by the peculiar arrangement of the voltaic apparatus, is transferred to the conducting wire and thence to the decomposing cell, where it effects the decomposition of the electrolyte. The required amount of energy may of course be supplied in other ways, *e.g.* the application of muscular power or steam-power to drive a magneto-electric machine, &c.

Mercury heated in the air nearly to its boiling point takes up oxygen, forming red mercuric oxide, which at a higher temperature is resolved into its elements. In this combination of the oxygen and mercury is attended with evolution of heat (though, in the peculiar circumstances of the reaction, it is not directly observable), inasmuch as the oxygen has passed from the gaseous and the mercury from the liquid, into the solid state. This quantity of heat is restored by raising the mercuric oxide to a high temperature, and then the compound decomposes.

When 2 volumes of ammonia gas are passed through a red-hot tube, they are resolved into 4 volumes of permanent gases. Now the formation of ammonia (which cannot be effected directly) must have been attended with evolution of heat: 1. because condensation has taken place; 2. because two elements which are permanent gases in the free state, have passed into the less volatile form of ammonia. The heat thus lost in combination is restored by passing the ammonia gas through the red-hot tube.

Marsh-gas,  $\text{CH}_4 = 16$ , gives out in burning 209,008 heat-units. On the other hand:

1 at. carbon gives out .	25,960 heat-units
4 at. hydrogen „ .	137,942 „
together	234,808 „
Subtracting the above .	209,008 „
there remains .	25,800 „

Hence it appears that marsh-gas in burning evolves 25,800 heat-units less than its elements. If, now, 1 volume of marsh-gas be passed through a white-hot tube, it is resolved into 2 vol. hydrogen and a small quantity of carbon. Here, then, is a proof that marsh-gas, in condensing into half the volume which the contained hydrogen would occupy in the free state, has sustained a loss of molecular movement. If the elements are burnt after separation, they again give out the entire amount of 234,808 heat-units; they must, therefore, in separating have regained this amount of molecular movement.

Thermolysis takes place with greater facility in proportion as the elements of a compound differ more widely from one another in their chemical characters; thus, the antimonide of hydrogen is decomposed by heat more easily than the arsenide, and this more readily than the sulphide.

The oxides of the noble metals are very easily resolved into their elements by heat. When such an oxide is reduced by hydrogen, less heat is produced than when the hydrogen combines with free oxygen, because the latter, in its state of combination, as oxide has lost its gaseous form, and the molecular movement belonging thereto.

The peroxides of lead and manganese are resolved by heat into free oxygen and lower oxides; and it is conceivable that at a higher temperature they might be resolved into oxygen and metal.

Carbon bisulphide is resolved, by the heat of an electro-ignited platinum-spiral, into sulphur and carbon, the decomposition being, however, attended, not with absorption, but with emission of heat. This apparent anomaly is explained by the fact that the carbon and sulphur, in combining together at a white heat, pass from the solid to the gaseous state, and absorb heat. A gram of carbon bisulphide in burning in oxygen develops 222 units of heat more than its elements in the free state: it must, therefore, in the act of combination have taken up molecular movement; and it is in consequence of this that the compound is much more volatile than either of its constituents.

Many salts, such as the carbonates, containing volatile acids, are directly resolved by heat into acid and base, and the facility with which they are so resolved is greater as the heat evolved in their formation is less.

The formation of barium carbonate is attended with a greater evolution of heat than that of calcium carbonate, and that of calcium carbonate with a greater evolution of heat than that of magnesium carbonate: on the other hand, magnesium carbonate gives off its carbonic anhydride at a low red heat, calcium carbonate at a cherry-red heat, and barium carbonate only at very high temperatures, so that, indeed, it was long regarded as undecomposable by heat. This example shows clearly that the quantity of heat required for the decomposition of a compound is intimately related to that which has been evolved in its formation.

The same relation is seen in the formation and decomposition of hydrates. Anhydrous potassium oxide, in uniting with water, evolves a very large quantity of heat, the oxide formed when a globule of potassium burns on the surface of water, sinking into the water with explosion; on the other hand, the water in the hydrate is absolutely fixed, and cannot be expelled by any degree of heat, the hydrate volatilising undecomposed at a cherry-red heat. Anhydrous baryta becomes red-hot in combining with water, and the water cannot be expelled from the hydrate by heat. Lime, in combining with water, also evolves a considerable quantity of heat, though less than baryta, and the hydrate gives up its water at a strong red heat. Anhydrous cupric sulphate emits great heat in uniting with 1 mol. of water, less in combining with 4 other molecules; and accordingly these four are given off below the boiling point of water, the fifth only at a red heat.

Sulphuric anhydride unites with 1 mol. of water with passing and explosion, and the hydrate  $\text{SO}_3 \cdot \text{H}_2\text{O}$  cannot be decomposed by heat, but distils as a whole. The boiling point of the water has risen by the combination from  $100^\circ$  to  $328^\circ$ , that of the sulphuric anhydride from  $52^\circ$  to  $328^\circ$ . Now when a body becomes less volatile it must have lost molecular motion. Consequently, rise of boiling point and emission of heat are intimately connected, although in the case just cited a solid body ( $80^\circ$ ) has passed into the liquid state.

The main points in the theory of Thermolysis may be summarised as follows:—

1. Thermolysis or Dissociation is the process opposite to chemical combination: the gaseous constituent of the compound resuming its molecular movement in the form of heat, and transforming it into a new form of movement which it had lost in the act of combination.
2. The quantity of heat taken up by the separated constituents is equal to that which they had lost in combining.
3. Compounds not containing any volatile constituent cannot be decomposed by heat.\*

**Radiant Heat. Diathermancy.**—Only a few substances are known which, in thick as well as in thin layers, transmit more than half of the heat emitted by lamp-black at  $100^\circ$ . Those substances are partly elements, viz., iodine in solution, bromine, and sulphur; partly chlorides, fluorides, and sulphides, viz. rock-salt, fluorspar, carbon sulphide, and sylvin. It appears, however, from the experiments of Schulz-Sellack (*Pogg. Ann.* cxxxix, 182) that not only all chlorides, but likewise the bromides, iodides, and fluorides of the elementary bodies, besides a number of sulphides, transmit a considerable proportion of the heat emitted by lamp-black. The percentage of the total quantity of heat transmitted by the several substances is shown in the following table:—

\* Views similar to the above have been developed by Odling in a lecture on *Reverse Chemical Action* delivered before the British Association at Norwich in 1868. See 'A History of Chemical Theory,' by A. Watts, translated by H. Watts, note A, p. 218.

Diathermanous substance	Thickness	Quantity of heat transmitted	
		Lamp-black at 100°	Coal-gas flame
Silver chloride . . . . .	3 mm.	46 p.c.	30 p.c.
Silver bromide . . . . .	3	45	42
Potassium bromide . . . . .	3	16	13
Potassium iodide . . . . .	3	11	10
Cryolite . . . . .	10	7	23
Zinc-blende . . . . .	5	29	23
Arsenious sulphide, $As_2S_3$ . . . . .	0·8	21	26
	3	8	12
	0·4	50	36
Vitreous Selenium . . . . .	3	16	5

Most of the substances examined, however, were not perfectly homogeneous, so that part of the heat must have been lost by diffusion and reflection.

A number of liquid compounds and solutions of substances which could not be obtained in the solid form in a fit state for experiment, were examined in a layer 8mm. thick in a glass vessel closed with parallel plates of rock-salt 2mm. thick. The following numbers show the quantities of heat transmitted through the filled vessel in percentages of the quantity passing through the empty vessel; but like those in the preceding table, they do not exhibit the absolute values of the absorption :—

Diathermanous Substance	Transmitted Heat	
	Lamp-black at 100°	Coal-gas flame
Stannic chloride, $SnCl_4$ . . . . .	44 p.c.	80 p.c.
Sulphur chloride, $SCl_2$ . . . . .	41	95
Carbon bisulphide . . . . .	50	51
10 parts Phosphorus in 1 part Carbon bisulphide . . . . .	52	57
1·5 part Stannic iodide, $SnI_4$ , in 1 part Carbon bisulphide . . . . .	44	47
1 part Carbon trichloride, $CCl_4$ , in 4 parts Carbon bisulphide . . . . .	5	38
Chloroform . . . . .	2	30
Ethylene chloride, $C_2H_4Cl_2$ . . . . .	0	12
Ethyl iodide, $C_2H_5I$ . . . . .	0	12

*Distribution of Heat in the Solar Spectrum and in the Spectrum of the Lime-light.*—

From experiments by S. Lamansky (*Berl. Acad. Ber.* 1871, 632) it appears that the strong heat observed in the bright part of the lime-light spectrum proceeds chiefly from heat-rays which have been bent from their course by diffuse reflection in the rock-salt prisms, as in turbid media. The law established by Melloni's experiments that the ultra-red rays in passing through transparent bodies (as water, glass, mica, quartz, calcspar) suffer a loss which is greater as their refrangibility is less, is shown by Lamansky's observations, made at different hours of the forenoon, to apply also to the absorption of these rays by atmospheric air.

**Conduction of Heat.** a. *In Gases.*—F. Narr (*Pogg. Ann.* cxlii. 123) has made experiments on heat-conduction and the rate of cooling in hydrogen, nitrogen, air and carbon dioxide, from which the following conclusions are drawn :—(1). The mathematical expression given by Dulong & Petit (v. 53), does not express the true law of the variation of the rate of cooling of a heated body in a gas with the temperature, inasmuch as it gives only the cooling effect of the gas. (2). The cooling effects of different gases differ very considerably, and gases must be ranged, with respect to this effect, not according to their chemical but rather according to their physical character, since hydrogen and carbon dioxide—two gases differing very widely in specific gravity and in capacity for heat—likewise exhibit the greatest difference of cooling power, whereas nitrogen and atmospheric air, which are characterised by almost identical

physical constants, likewise exhibit almost equal rates of cooling. (3). Calculations made to trace the dependence of the observed temperatures on the times of cooling by means of the formula,  $\log T - \log T = a_1x + a_2x^2$ , showed that in all cases the coefficient  $a_2$  has a very small value, which, with exception of the data of observation relating to hydrogen, was negative. Hence it appears that, for most gases, the deviations from Newton's law of the proportionality of the rate of cooling of a body to the excess of its temperature above surrounding objects (v. 52) are inconsiderable, and that hydrogen exhibits a deviation in the contrary sense. (4). Calculations relating to cooling in a vacuum give also a very small value for the coefficient  $a_2$ , so that the deviations of the rates of cooling calculated from the formula  $v = mT$  from the rates actually observed, were but slightly greater than those relating to cooling in hydrogen. For these reasons Nurr regards it as highly probable that Newton's law is the true expression for the cooling effect due to radiation alone.

Stofan (*Wien. Anzeig.*, 1872, 42; *Chem. Soc. J.* [2], x. 177), from experiments with double-walled thermometers of brass or copper-plate, having the space between the metallic envelopes filled with the gas under examination, concludes that the conducting power of air is nearly 20,000 times less than that of copper, and 3,400 times less than that of iron. His experiments confirm the conclusion deduced from the dynamical theory of gases, that the conducting power of any particular gas is independent of its density; also the conclusion deduced by Maxwell from the same theory, that the conducting power of hydrogen is seven times as great as that of air.

For F. Mohr's theoretical views on the heat-conducting power of gases, see *Dent. Chem. Ges. Ber.* iv. 85; *Chem. Soc. J.* [2], ix. 298.

*Conduction of Heat in Stratified Liquids.*—Experiments relating to this matter by Despretz have been published, since his death, by Saigey (*Compt. rend.* lxxii. 481; *Pogg. Ann.* clxii. 626). A wooden cylindrical vessel 72 centimeters high and 40 cm. in diameter, was half filled with nitrobenzene of sp. gr. 1.20, and water was poured on the top. Ten horizontal thermometers served for the observation of the stationary temperatures, whilst a constant source of heat acted on the surface of the water. In experiment 1, the bulbs of the thermometers were placed in the axis of the cylinder; in experiment 2, they reached only to the middle of its semi-diameter. The following table gives the distances of the thermometers from the surface of separation of the two liquids, and the excesses of the observed temperatures above the temperature of the surrounding atmosphere:—

Thermometers		Experiment No. 1		Experiment No. 2	
Water	A	133.7 mm.	41.26°	137.44 mm.	41.15°
	B	101.8	31.17	110.34	32.01
	C	69.1	23.62	80.25	24.76
	D	41.5	18.66	49.25	19.16
	E	17.5	15.68	15.90	14.83
Nitro-benzene	F	17.5	11.83	15.90	10.68
	G	46.6	7.09	41.90	6.84
	H	75.7	4.48	60.80	4.36
	I	106.2	2.56	101.40	2.43
	K	138.6	1.50	133.00	1.11

On tracing the curves corresponding with these numbers, taking the distances as abscissæ and the excess of temperature as ordinates, it is found that, for equal distances, the ordinates are nearly in geometric proportion. If the distances be taken at 17.5 mm., the mean ratio of the successive ordinates is:

	Experiment 1	Experiment 2
In Water	0.881	0.863
In Nitro-benzene	0.739	0.703

At the boundary of the two liquids, Despretz had unfortunately not placed any thermometers. Here the two curves separate; from the water to the nitro-benzene, which conducts on the average 3.7 times less easily, the calculated temperature rises about 2° or 2.5°.

**HELICIN.** This body treated with phosphorus oxychloride, is for the most part converted into glucoso-phosphoric acid (p. 561).



**HELLEBORE.** The constituents of white hellebore-root have been examined by H. Weppen (*Arch. Pharm.* [3], ii. 101, 193), who has obtained from it a bitter substance called *veratramarin*, and an acid called *jervic acid*.

*Veratramarin* exists in aqueous extracts of the root after the separation of the alkaloids, imparting to them its bitter taste. To obtain it, the sliced root was macerated with cold lime-water, the infusion was freed from lime by means of carbonic acid, and the filtered liquid was mixed with excess of neutral lead acetate and again filtered. The bitter-tasting liquid thus obtained, on standing for some days, deposited on the sides of the vessel a brown crystalline crust (see below). The liquid decanted from this deposit was precipitated with a slight excess of basic lead acetate; the precipitate containing the whole of the bitter substance was decomposed, after thorough washing, by hydrogen sulphide; and the filtered liquid, after boiling to expel excess of the gas, and cooling, was mixed with solution of tannin. The precipitate thereby produced was washed, mixed with lead hydrate, evaporated to dryness over the water-bath, and then exhausted with 40 p.c. alcohol. The pale yellow-body left on distilling off the alcohol, proved to be too small in quantity to admit of full investigation. It appears to be extremely unstable and probably undergoes decomposition during preparation. It reduces alkaline solutions of copper after boiling with acids but not before, and hence appears to be a glucoside. It is soluble in water, but insoluble in ether, benzene, and chloroform, which circumstance makes it difficult to isolate. It is very hygroscopic, deliquescent in the air in a few minutes, and rapidly turning dark brown.

*Jervic acid*,  $C^{14}H^{10}O^{12} + 2H^2O$ .—The crystalline body above referred to, which was found to be a lead-salt, was suspended in water and decomposed by hydrogen sulphide; and the acid liquid, filtered hot, was evaporated, leaving a mass of crystals which, after purification, formed a white, light crystalline powder not obtainable in large crystals. This body is *jervic acid*. It is soluble in 10 parts of hot and 100 parts of cold water, sparingly soluble in alcohol and ether, insoluble in benzene, carbon sulphide, chloroform, amyl alcohol, and dilute acids. It gives with neutral and basic lead acetates, precipitates insoluble in acetic but soluble in nitric and hydrochloric acids; with silver nitrate a white precipitate, soluble in ammonia and unaltered by exposure to light; with mercurous nitrate a brilliant white crystalline precipitate, insoluble in water but soluble in nitric acid. With baryta- and lime-water it gives white precipitates which turn yellow after some time.

*Jervic acid* is quaternary basic. Its potassium and sodium salts are obtained by neutralising an aqueous solution of the acid with the pure carbonates and evaporating over sulphuric acid. They are both very soluble in water, and have an alkaline reaction.

The barium salt is a heavy, glittering crystalline powder, consisting of six-sided tables. The strontium salt is a crystalline powder, rather more soluble than the barium salt.

Calcium *jervate* crystallises more distinctly in four- or six-sided rhombic prisms. There are two silver salts, both obtained by precipitation; also a mercurous salt in the form of a crystalline powder.

The composition of these salts is represented by the following formulae:—

Potassium <i>jervate</i>	. . .	$K^4C^{14}H^{10}O^{12} + 2H^2O$
Sodium "	. . .	$Na^4C^{14}H^{10}O^{12} + 3H^2O$
Barium "	. . .	$Ba^2C^{14}H^{10}O^{12}$
Strontium "	. . .	$Sr^2C^{14}H^{10}O^{12} + H^2O$
Calcium "	. . .	$Ca^2C^{14}H^{10}O^{12} + 6H^2O$
Acid silver	. . .	$Ag^2C^{14}H^{10}O^{12} + 2H^2O$
Neutral silver	. . .	$Ag^4C^{14}H^{10}O^{12}$
Mercurous "	. . .	$Hg^4C^{14}H^{10}O^{12} + 4H^2O$

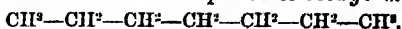
*Jervic acid* is coloured yellow by alkalis. When boiled with baryta-water, it yields a crystallisable acid, the examination of which is not yet completed.

**HELVIN.** N. von Kokschnrow (*Jahresb. f. Chem.* 1860, 1228) describes helvin: 1. From Miask in the Ilmen Mountains, in spherical masses, some as big as a man's head; sp. gr. 3.333. 2. From Lupiko in Finland, in crystals,  $\frac{202}{2}$ , some more than an inch long; sp. gr. = 3.23 to 3.37. Analyses of two specimens from each locality have been made by N. Teich:

	SiO <sup>2</sup>	AlF <sup>3</sup>	GO	FeO	MnO	CaO	MgO	S	H <sup>2</sup> O	
1.	{ 32.67	0.76	18.67	15.03	35.51	—	—	—	—	= 97.43.
	{ 32.42	0.78	18.46	15.21	35.31	—	—	5.77	—	= 102.96.
2.	{ 30.31	—	10.51	10.37	37.87	4.03	0.60	5.95	0.22	= 99.25.
	{ 33.88	—	10.40	10.37	37.90	4.10	0.66	—	0.22	= 94.03.

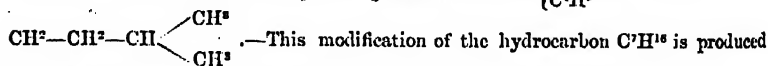
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T T

**HEPTAMINE-CHROMIUM COMPOUNDS.** See CHROMIUM (p. 336).**HEPTANES, C<sup>7</sup>H<sup>16</sup>.** *a. Normal Heptane or Heptyl-methane,*

occurs, together with other paraffins, in Pennsylvanian petroleum and in the light oils obtained from cannel- and Boghead-tar. When separated as completely as possible by fractional distillation, it boils at 97.5°-98°, not at 92°-94° as stated by Pelouze & Cahours. When chlorine is passed into its vapour at the boiling heat, two isomeric heptyl chlorides are obtained, which boil at 145°-160°, and are converted, by heating to 200° with potassium acetate and glacial acetic acid, into the corresponding heptyl acetates boiling at 175°-185°. Neither the chlorides nor the acetates can be separated by fractional distillation, but by heating the mixed acetates with potash they are converted into heptyl alcohols, the mixture of which can be separated by fractional distillation into a primary and a secondary heptyl alcohol, each having a nearly constant boiling point, though still not quite pure. The primary heptyl alcohol thus obtained boils at 170°-175°, and is converted by oxidation into *enanthylic acid*, C<sup>7</sup>H<sup>14</sup>O<sup>2</sup>, boiling at 219°-222°, and identical with that which is prepared from castor-oil. The secondary heptyl alcohol boils at 160°-162°, and is converted by oxidation into methyl-pentyl ketone, CO {CH<sup>3</sup>/<sub>C<sup>2</sup>H<sup>5</sup></sub>}, boiling at 150°-152°. The secondary alcohol is there-

fore methyl-pentyl carbinol, {CH<sup>3</sup>/<sub>C<sup>2</sup>H<sup>5</sup></sub>} CH.OH. The ketone is converted by further oxidation into acetic and normal valeric acid, CH<sup>3</sup>-(CH<sup>2</sup>)<sup>3</sup>-COOH, showing that the heptane from which these derivatives have been obtained is the normal compound CH<sup>3</sup>-(CH<sup>2</sup>)<sup>5</sup>-CH<sup>3</sup>.

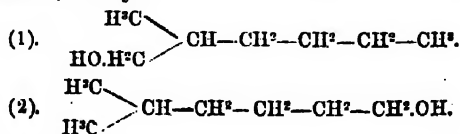
*B. Ethyl-amyl or Dimethyl-butylmethane,* CH {CH<sup>3</sup>/<sub>C<sup>4</sup>H<sup>9</sup></sub>}, or CH<sup>3</sup>-CH<sup>2</sup>-

by the action of sodium on a mixture of the bromides or iodides of ethyl and amyl (1st Suppl. 696). Grimshaw (*Chem. Soc. J.* [2], xi. 309) prepares it by gradually adding sodium to a mixture of the bromides contained in a flask with reversed condenser, in such proportion as to keep the liquid at 25°-26° by heating it to 100° for some hours, and afterwards distilling off. The mixture of hydrocarbons thus obtained is left standing for some weeks over sodium, then repeatedly rectified over sodium and fractionally distilled, and finally purified by treatment with strong nitric and sulphuric acid, washing with water, leaving it in contact for 48 hours with sticks of potash, again distilling it with sodium, and then leaving it in contact for a week or two with sticks of potash.

The ethyl-amyl thus prepared boiled constantly at 90° and had a specific gravity of 0.6823 at 18.4°. By the action of chlorine on its vapour at the boiling heat, a mixture of chlorides was obtained which did not give any constant boiling point, but yet distilled almost entirely within about 10°. This mixture yielded, by the action of potassium acetate and acetic acid, a liquid which also could not be obtained of constant boiling point, but distilled within about 15°. From this, however, a mixture of alcohols was obtained, of which a more or less complete separation could be effected into a primary alcohol boiling at 165°, and a secondary alcohol boiling at about 147°.

The primary alcohol thus obtained is an iso-heptyl alcohol, as shown by its boiling point, which is about 10° lower than that of normal heptyl alcohol, and by the fact that it is converted by oxidation into an iso-*enanthylic acid*, C<sup>7</sup>H<sup>14</sup>O<sup>2</sup>, boiling at 210°-213°, that is to say, 8° or 10° lower than normal *enanthylic acid*.

Now, as ethyl-amyl contains three methyl-groups, two isomeric primary alcohols may be derived from it, namely:



It is for the present impossible to decide which of these two formulæ expresses the true constitution, but the second formula is perhaps the more probable.

The secondary alcohol is methyl-isoamyl-carbinol, CH {CH<sup>3</sup>/<sub>C<sup>2</sup>H<sup>5</sup></sub>} CH {CH<sup>3</sup>/<sub>C<sup>2</sup>H<sup>5</sup></sub>} CH.OH, as is proved by the fact of its yielding by oxidation methyl-isoamyl ketone,

$\text{CH}_3\text{--CO--C}^2\text{H}^{11}$ , boiling at  $143^\circ\text{--}145^\circ$ , and identical with that which Popoff obtained (*Zeitschr. f. Chem.* 1865, 577) by the action of zinc-amyl (from ordinary amyl alcohol) on acetyl chloride.

$\gamma$ . *Dimethyl-diethylmethane*,  $\text{C}\left\{\begin{smallmatrix} \text{CH}_3 \\ \text{C}^2\text{H}_5 \end{smallmatrix}\right\}_2$ .—This modification is contained, together with normal heptane and other hydrocarbons, in Pennsylvanian petroleum. After separation by fractional distillation, it boils at  $89.5^\circ$  to  $90^\circ$ . Like normal heptane and ethyl-amyl, it yields by chlorination, &c., two series of derivatives, the boiling points of which differ in some cases from those obtained from ethyl-amyl:—

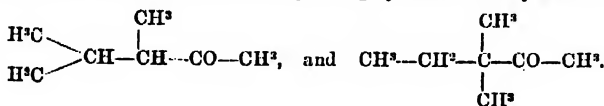
	Derivatives of the hydrocarbon from petroleum	Derivatives of ethyl-amyl
Paraffin, $\text{C}^7\text{H}^{16}$ . . . . .	$89.5^\circ\text{--}90^\circ$	$90^\circ$
Olefine, $\text{C}^7\text{H}^{14}$ . . . . .	$90^\circ\text{--}92^\circ$	$91^\circ$
Chloride, $\text{C}^7\text{H}^{13}\text{Cl}$ . . . . .	$144^\circ\text{--}158^\circ$	$140^\circ\text{--}150^\circ$
Acetate, $\left\{\begin{smallmatrix} \text{C}^7\text{H}^{13} \\ \text{C}^7\text{H}^{13}\text{O} \end{smallmatrix}\right\}\text{O}$ . . . . .	$160^\circ\text{--}185^\circ$	$160^\circ\text{--}175^\circ$
Alcohol, $\left\{\begin{smallmatrix} \text{C}^7\text{H}^{15} \\ \text{H} \end{smallmatrix}\right\}\text{O}$ . . . . .	Primary $165^\circ\text{--}170^\circ$ Secondary $148^\circ\text{--}150^\circ$	$163^\circ\text{--}165^\circ$ $146^\circ\text{--}148^\circ$
Ketone, $\text{C}^7\text{H}^{14}\text{O}$ . . . . .	$142^\circ\text{--}146^\circ$	$143^\circ\text{--}145^\circ$
Acid, $\text{C}^7\text{H}^{14}\text{O}_2$ . . . . .	$209^\circ\text{--}213^\circ$	$210^\circ\text{--}213^\circ$

The heptane,  $\text{C}^7\text{H}^{14}$ , was obtained in both cases as a secondary product in the preparation of the acetate from the chloride.

The acid  $\text{C}^7\text{H}^{14}\text{O}_2$ , derived from the  $\gamma$  heptane, boils at the same temperature as iso-cenanthylic acid, and has a very similar smell; its salts also resemble the corresponding iso-cenanthylates. The silver salt,  $\text{C}^7\text{H}^{13}\text{AgO}_2$ , is a flocculent crystalline precipitate. The barium salt does not crystallise, but forms an amorphous mass, like barium iso-cenanthylate. The calcium salt separated, on evaporating its solution by heat, as an amorphous pollicle, but by spontaneous evaporation it was obtained in long, transparent needles or prisms.

The ketone,  $\text{C}^7\text{H}^{14}\text{O}$ , boils at the same temperature as methyl-isoamyl ketone, and smells very like the latter compound; but on oxidising it, a marked difference between the two compounds is observed. Methyl-isoamyl ketone yields, by oxidation, acetic and valeric acids, whereas the ketone derived from  $\gamma$  heptane yields nothing but acetic acid.

Now Popoff has shown that when a ketone is oxidised, the lower, or more stable, of the alcohol-radicles always remains attached to the carbonyl, while the other radicle is oxidised just as its alcohol would be (1st Suppl. 765). According to this law there may exist two ketones,  $\text{C}^7\text{H}^{14}\text{O}$ , yielding by oxidation only acetic acid, viz:



The first of these two ketones will in the first instance be resolved into acetic acid and methyl-isopropyl ketone, and the latter will yield by further oxidation acetic acid and dimethyl ketone, which will finally be also oxidised to acetic acid.

The second ketone must, according to Popoff's law, yield acetic acid and the oxidation-products of tertiary amyl. But the latter also consist only of acetic acid: for Butlerow has shown that, on oxidising a tertiary alcohol, the most simple radicle always remains combined with the carbon-atom by which the whole group is kept together, whilst the two other radicles are oxidised separately; and experiment has proved that tertiary amyl alcohol, or dimethyl-ethyl carbinol, is oxidised completely to acetic acid.

The first of the ketones is a derivative of *methyl-ethyl-isopropylmethane*,  $\text{CH}\left\{\begin{smallmatrix} \text{CH}_3 \\ \text{C}^2\text{H}_5 \end{smallmatrix}\right\}_2$ , a paraffin which is not yet known; whilst the second ketone is

derived from *dimethyl-diethylmethane* or *carbodimethyldiethyl*,  $\text{C}\left\{\begin{smallmatrix} \text{CH}_3 \\ \text{C}^2\text{H}_5 \end{smallmatrix}\right\}_2$ , which compound Friedel and Ladenburg prepared by the action of zinc-ethyl on dimethyl-dichloromethane  $\text{CCl}_2(\text{CH}_3)_2$  (1st Suppl. 826).

At present it is impossible to decide with certainty with which of these two paraffins  $\gamma$  heptane is identical, the quantity of the ketone obtained having been too small to allow of the isolation of the intermediate products of oxidation, which would elucidate

its constitution, and therefore that of the paraffin. The properties of  $\gamma$  heptane agree, however, with those of dimethyl-diethylmethane sufficiently to render their identity not improbable. The latter paraffin boils at  $86^{\circ}$ – $87^{\circ}$ , and has at  $20.6^{\circ}$  the specific gravity 0.6968, whilst the hydrocarbon from petroleum boils at  $89.5^{\circ}$ – $90^{\circ}$ , and has at  $16^{\circ}$  the specific gravity 0.709. The higher boiling point of the latter is caused, partly at least, by an admixture of normal heptane boiling at  $98^{\circ}$  (Schorlemmer, *Chem. Soc. J.* [2], xi. 319).

**HEPTENE-CHLORHYDRIN**,  $C^7H^{13}(OH)Cl$ , is formed, together with other products, by treating octene with a 2 to 3 p.c. solution of hypochlorous acid, which, in a solution of this strength, exerts an oxidising as well as a reducing action. By fractional distillation the heptene-compound may be separated, boiling at  $206^{\circ}$ – $208^{\circ}$ . A weaker solution of hypochlorous acid ( $\frac{3}{4}$  p.c.) forms chiefly octene-chlorhydrin (P. de Clermont, *Bull. Soc. Chim.* [2], xiii. 404).

**HEPTYL ALCOHOL**,  $C^7H^{14}O$ . Normal *Heptyl alcohol*,  $CH^3-CH^2-CH^2-CH^2-CH^2-CH^2-CH^2-OH$ , may be advantageously prepared from *canthol*,  $C^7H^{14}O$ , by the action of sodium-amalgam. *Canthol* is shaken with fifty times its weight of water, and a little more than the required quantity of an amalgam containing 1 per cent. of sodium is added, together with an equivalent quantity of dilute sulphuric acid, care being taken to keep the liquid always slightly acid. As soon as the action is over, the liquid is distilled, and the distillate again treated in the same way with the amalgam. The alcohol floating on the top is then removed, and the portion remaining in the aqueous solution is isolated by repeated distillation, the alcohol always coming over with the first portion, from which it may be finally separated by adding potassium carbonate. The product is dried over ignited potassium carbonate, and the alcohol separated from another very high-boiling liquid by fractional distillation. To get rid of some *canthol* and water still present, the liquid is several times distilled over small pieces of sodium, and then left for several weeks in contact with anhydrous baryta.

Normal heptyl alcohol thus prepared is a limpid oily liquid, having an aromatic odour, and boiling under a pressure of 766 mm. at  $175.5^{\circ}$ – $177.5^{\circ}$ , the whole column of mercury being surrounded by the vapour (Grimshaw & Schorlemmer, *Chem. Soc. J.* [2], xi. 1081).

**HEPTYLIC ACID and ALDEHYDE.** See *Canthol*. **HEPTYLIC ACID and ALDEHYDE.**

**HERACLEUM.** The volatile oil of *Heracleum giganteum* is a mixture of octyl acetate and the hexylic ether of normal butyric acid. By saponifying the greater portion of the oil which passes over between  $200^{\circ}$  and  $206^{\circ}$  with caustic potash, and fractional distillation, the two alcohols may be obtained in the pure state. The octyl alcohol is identical with that which is prepared from the oil of *Heracleum sphondylium* (1st Suppl. 697). The hexyl alcohol will be described further on (Franchimont & Zincke, *Deut. Chem. Ges. Ber.* iv. 822).

**HESPERIDENE.** The terpene of essential oil of orange-peel. (See TERPENES).

**HETEROGENITE.** A hydrated cobaltoso-cobaltic oxide occurring, together with calc spar and pharmacolite, in the nickel and cobalt veins of the Wolfgang Maessen mine at Schneeberg in Saxony. It is amorphous, and occurs in botryoidal and kidney-shaped masses, having a dense fracture. Lustre faint. Colour blackish to reddish-brown: the ignited powder is coal-black. Streak dark-brown, with a fatty lustre. Hardness equal to that of calc spar. Sp. gr. 3.44.

Its blowpipe reactions are as follows:—It gives off water when heated in a tube; heated in the forceps it melts with difficulty on the edges, and colours the flame slightly green; appears slightly magnetic after ignition; exhibits cobalt reaction with glass fluxes. It dissolves easily in hydrochloric acid, giving off chlorine and leaving an insoluble residue; the green solution turns red when heated, and gives with ammonia a small precipitate of ferric oxide.

The quantitative analysis of two specimens gave:

	CoO	O	CaO	CoO'	FeO'	AlO'	CaO	MgO	H <sup>2</sup> O	Residue	
a	59.03	5.03	0.60	0.35	1.20	1.30	1.60	0.45	14.56	16.00	= 100.12
b	39.94	2.81	0.56	0.32	0.80	—	3.60	2.02	12.25	32.20	= 103.50

Most of these constituents are foreign to the mineral, and on deducting them—namely the insoluble residue, consisting mainly of silica, which remains on dissolving the mineral in acids, as a skeleton made up of large flocks—also the oxides of iron, copper, bismuth, calcium, and magnesium—there remains for the composition of the heterogenite—

CoO	O	H <sup>2</sup> O	or	CoO	Co <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O
75.17	6.41	18.54		14.32	67.26	18.54
68.83	5.51	24.13		16.24	58.13	24.13

agreeing nearly with the formula,  $\text{CoO} \cdot 2\text{Co}^2\text{O}^3 + 6\text{H}^2\text{O}$ , which requires 14.61 p.c. CoO, 61.61 Co<sup>2</sup>O<sup>3</sup>, and 20.78 water.

Hoterogenite was originally mistaken for asbolan or earthy cobalt—a manganese ore—and, in fact, it exhibits a distinct trace of manganese when fused with sodium carbonate and nitro. One specimen was found to contain nickel in the proportion of 1 part nickel to 20 parts cobalt.

Hoterogenite is a product of the decomposition of smaltine or tin-white cobalt (speiss-cobalt); it is interesting as the first mineral in which the amount of cobalt existing as sesquioxide has been actually determined (A. Frenzel, *J. pr. Chem.* [2], v. 404).

#### HEXAMIDO- and HEXNITRO-ALBUMIN-SULPHONIC ACIDS.

When dried albumin is treated with a mixture of concentrated nitric and sulphuric acids in the cold, and the mixture, after standing for several hours, is thrown into cold water, a precipitate is thrown down, which, when dried, forms three-fourths of the albumin originally taken. It is a bitter, yellow powder, insoluble in water, alcohol, and dilute acids; soluble in dilute alkalis, forming a red solution, from which it may be reprecipitated unchanged. Assuming the formula of albumin to be  $\text{C}^{72}\text{H}^{108}\text{N}^{18}\text{SO}^{22}$ , the new substance is *hexanitro-albuminsulphonic acid*,  $\text{C}^{72}\text{H}^{101}(\text{NO}^2)^6(\text{SO}^2\text{OH})\text{N}^{18}\text{SO}^{22}$ . On treating this body with ammonium sulphide, *hexamido-albuminsulphonic acid*,  $\text{C}^{72}\text{H}^{101}(\text{NH}^2)^6(\text{SO}^2\text{OH})\text{N}^{18}\text{SO}^{22}$  is formed, as a brownish-yellow powder, having a faint taste, soluble in dilute alkalis, decomposed by strong alkalis, especially on warming, with evolution of ammonia. Nitric acid dissolves it, with evolution of red fumes. It is insoluble in dilute acids, but when freshly precipitated, dissolves readily in concentrated acids (O. Loew, *J. pr. Chem.* [2], iii, 180).

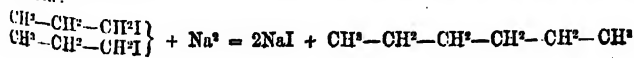
#### HEXAMINE- (or TRIAMINE-) CHROMIUM-COMPOUNDS. (See p. 336.)

**HEXANES**,  $\text{C}_6\text{H}_{14}$ . (Schorlemmer, *Phil. Trans.* 1872, 111). *Normal hexane*,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ , occurs, together with other paraffins, in Pennsylvanian petroleum and in the light oils from Boghead and cannol coal. It boils at  $60^\circ\text{--}70^\circ$ . When chlorine is passed into its vapour at the boiling heat, a mixture of hexyl chlorides is produced, the greater part of which distils constantly at  $125^\circ\text{--}126^\circ$ . Treated with potassium acetate they yield hexene,  $\text{C}_6\text{H}_{12}$ , boiling at  $69^\circ\text{--}70^\circ$ , and hexyl acetates distilling between  $158^\circ$  and  $160^\circ$  (not at  $145^\circ$ , as stated by Pelouze and Colours). The secondary alcohol obtained from these mixed acetates is methyl-

butyl carbinol  $\begin{matrix} \text{CH}_3 \\ | \\ \text{C}_6\text{H}_{13} \end{matrix} \cdot \text{CH}_2\text{OH}$ , yielding by oxidation methyl-butyl ketone, boiling at  $126^\circ\text{--}128^\circ$ , and then acetic and *normal* butyric acid. The primary hexyl alcohol obtained from the same mixture of acetates boils at  $150^\circ\text{--}155^\circ$ , and is converted by oxidation into caproic acid, which boils at  $200^\circ\text{--}205^\circ$ , and yields a silver salt crystallising in needles, and a calcium salt in shining scales or ramified needles: its barium salt forms an amorphous mass.

*Normal hexane* is also produced by the action of zinc and dilute hydrochloric acid on secondary hexyl iodide (methyl-butyl iodide) obtained from mannite. The product contains, besides hexane, small quantities of hexene and dihexyl or dodecane  $\text{C}_{12}\text{H}_{26}$ . The latter, which boils at  $202^\circ$ , may be removed by distillation, and the hexene by means of bromine. The purer hexane thus prepared boils constantly at  $171.5^\circ$ , and has a specific gravity of 0.6630 at  $17^\circ$ . The chlorides obtained from it boil at  $126^\circ\text{--}130^\circ$ , and yield a mixture of two hexyl alcohols, viz., methyl-butyl carbinol, boiling at  $140^\circ\text{--}141^\circ$ , and yielding by oxidation *normal* butyric acid, and a primary alcohol which boils at  $150^\circ\text{--}153^\circ$  and is converted by oxidation into a caproic acid boiling at  $201^\circ\text{--}204^\circ$  and exhibiting properties similar to the caproic acid derived from petroleum, excepting that the acid from mannite gives a well-crystallised barium salt. The hexane from mannite and some of its derivatives also boil at a few degrees higher than the corresponding petroleum derivatives. These differences are probably due to the presence of small quantities of other paraffins in the hexane from petroleum. The formation of acetic and of *normal* butyric acid from the hexanes from petroleum and from mannite show indeed that both have the constitution of a normal paraffin.

*Dipropyl*,  $\text{C}_3\text{H}_7 \cdot \text{C}_3\text{H}_7$ , prepared from normal propyl iodide,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{I}$ , (boiling at  $102^\circ\text{--}103^\circ$ ) by heating a mixture of this iodide and anhydrous ether with sodium to  $140^\circ\text{--}150^\circ$ , is likewise identical in physical properties with the hexane from the two sources above mentioned. The identity is further shown by its mode of formation:



$\text{HC}(\text{CH}_3)_2$   
*Tetramethyl-ethane*,  $\begin{array}{c} \text{HC}(\text{CH}_3)_2 \\ | \\ \text{HC}(\text{CH}_3)_2 \end{array}$ .—This modification of hexane is derived from

pinacene,  $\text{C}^8\text{H}^{10}\text{O}^2$ , which is formed by the action of sodium-amalgam on aqueous acetone, and has the constitution of tetramethylated ethene glycol (iv. 647; 1st *Suppl.* 946). Pinacene boiled with iodine and phosphorus in presence of water, or heated in sealed tubes with hydriodic acid, yields a mixture of pinacolin,  $\text{C}^6\text{H}^{12}\text{O}$  (anhydride of pinacene), an iodide,  $\text{C}^6\text{H}^{11}\text{I}$  (b. p.  $142^\circ$ – $145^\circ$ ), which constitutes three-fourths of the crude product, and small quantities of more condensed derivatives of acetone. The iodide,  $\text{C}^6\text{H}^{11}\text{I}$ , heated with hydriodic acid, gives, besides a little inflammable gas and several liquid hydrocarbons boiling at about  $130^\circ$ , a liquid hexane boiling at  $59^\circ$ , identical with the so-called hydride of dipropylene which Berthelot obtained by treating diallyl with hydriodic acid (Bouchardat, *Compt. rend.* lxxiv. 800).

**HEXHYDRO-ISOXYLENE**,  $\text{C}^6\text{H}^{16}$ . See **XYLENE**.

**HEXHYDROPHTEALIC ACID**. See **PHTEALIC ACID**.

**HEXETHYL-DISILICIC ETHER**. See **SILICIC ETHERS**.

**HEXOKETHYL-DIPHOSPHOPLATINOUS CHLORIDE**. See **PLATINUM-COMPOUNDS**.

**HEXOKYDIPHENYL**,  $\text{C}^{12}\text{H}^{10}\text{O}^4$ , is produced, together with methyl chloride, by heating hydrocerulignone with hydrochloric acid in sealed tubes (p. 377).

**HEXOKYANTHERAQUINONE**, or **TETRA-OKYANTHRAQUINONE**,  $\text{C}^{14}\text{H}^8\text{O}^4$ . This, according to Jaffé (*Deut. Chem. Ges. Ber.* 1870, 694), is the constitution of rufgallie acid (1st *Suppl.* 999), inasmuch as that acid when distilled with zinc-dust yields anthracene. The formation of rufgallie acid by heating galleic acid with sulphuric acid will accordingly be represented by the equation  $2\text{C}^8\text{H}^6\text{O}^3 = 2\text{H}^2\text{O} + \text{C}^{14}\text{H}^8\text{O}^4$ .

**HEXYL ALCOHOLS**. The essential oil of *Heracleum giganteum* yields by fractional distillation a liquid distilling between  $201^\circ$  and  $206^\circ$ , which is a mixture of hexyl butyrate and primary octyl acetate.

The hexyl alcohol thus obtained is a colourless oily liquid with a strong aromatic odour. Its sp. gr. at  $23^\circ = 0.819$ , and corrected boiling point  $156.6^\circ$ . The corresponding *hexyl iodide*,  $\text{C}^6\text{H}^{13}\text{I}$ , is a colourless liquid with a faint odour; sp. gr. at  $17.5^\circ = 1.4115$ ; boiling point  $179.5^\circ$ .

The *acetate*,  $\text{C}^6\text{H}^{13}\text{C}^2\text{H}_3\text{O}^2$ , is a colourless, oily liquid, having at  $17.5^\circ$  the sp. gr. 0.889, and boiling at  $168.7^\circ$ . The *caproate*,  $\text{C}^6\text{H}^{13}\text{C}^6\text{H}^{11}\text{O}^2$ , is an oily, almost scentless liquid. Sp. gr. at  $17.5^\circ = 0.865$ ; boiling point  $245.6^\circ$ .

On oxidation, this alcohol yields caproic acid, which boils at  $204.5^\circ$ – $205^\circ$ , and has, therefore, the same boiling point as Lieben's normal caproic acid. As this hexyl alcohol boils at a higher temperature than all other primary hexyl alcohols so far studied, and as the difference between its boiling point and that of normal amyl alcohol is  $19^\circ$ , it is most probably normal hexyl alcohol:  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$  (Franchimont a. Zincke, *Deut. Chem. Ges. Ber.* iv. 822).

The cyanide prepared from this alcohol in the usual way yields, by distillation with caustic potash, a heptylic or enanthylic acid which boils at  $223$ – $224^\circ$  under a pressure of 762.7 mm., has a sp. gr. of 0.9912 at  $24^\circ$ , and solidifies completely in a mixture of ice and salt, but liquefies entirely again at  $8^\circ$ . It is, in all probability, normal enanthylic acid (Franchimont, *ibid.* v. 786). See **ENANTHYLIC ACID**.

The hexyl-compounds derived from mannite and from dulcitol have been examined by O. Hocht (*Ann. Ch. Pharm.* clxv. 140), who finds them to be identical both in their physical and in their chemical properties. The alcohols from the two sources, when oxidised by chromic acid, both yield acetic and normal butyric acid: they have, therefore, the constitution of methyl-butyl carbinol  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}^4\text{H}_9 \end{array} \text{CH.OH}$ .

**HIBISCUS**. The *Hibiscus esculentus*, called in Egypt *Bammg*, is there cultivated as a garden vegetable, the unripe green fruits being cooked like French beans. The fruit dried at  $100^\circ$  contains 2 to 2.4 p.c. nitrogen. Like those of other malvaceous plants, it is rich in pectin, starch, and mucilage. The ash contains abundance of potash, soda, magnesia, phosphoric acid, sulphuric acid, and chlorine. The ripe seeds contain 2.4 to 2.5 p.c. nitrogen. The ash of the seed is constituted as follows:—

K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	SiO <sup>2</sup>	Cl	CO <sup>2</sup>
38.84	4.58	7.81	12.02	0.86	24.69	0.56	0.75	1.64	8.25 = 99.90

(O. Popp, *Arch. Pharm.* [2]. cxlv. 140).

**HIPPURIC ACID.** Experiments on the influence of various kinds of fodder on the secretion of hippuric acid in the urine of herbivora have been made by Hofmeister (*Landw. Versuchs-Stationen*, xiv. 458).

Sheep fed on clover-hay secreted as an average 5.3 grams only of hippuric acid in 24 hours, but when fed on meadow-hay they secreted an almost constant quantity of 30 grams. The addition of benzoic acid to the clover-hay gave rise to an increase in hippuric acid of rather more than the calculated weight, showing that clover does not in itself prevent the formation. The distillate and watery extract obtained on distilling meadow-hay with water, dried and given to sheep, produced no increase in hippuric acid, but the dried residue caused its secretion in almost the same proportion as the original hay.

Meadow-hay was then exhausted consecutively with water, alcohol, and 3 p.c. soda-ley. The alcoholic extract produced a slight increase in hippuric acid; the watery and alkaline extracts and the residue had no appreciable effect. The non-formation of hippuric acid from this residue is in opposition to the observations of Meissner, who, from experiments on rabbits, arrived at the conclusion that the formation of this acid was due to the digestion of some substance contained in the crude fibre, probably the cuticular membrane. That the nitrogenous constituents of the food do not wholly regulate the secretion of the acid is proved by the facts that the addition of rape-cake to the food has no action on its quantity, but only increases the urea, and that a much smaller quantity is formed by feeding with clover than with graminaceous plants.

Neither do the apomatic substances of the food seem to have much influence: for the alcoholic extract of meadow-hay, containing the greater part of the aromatic bodies, produced but a small quantity of hippuric acid, and Henneberg and Stolman found as much in the urine of oxen fed on oat-straw as in that of oxen eating meadow-hay.

By gradually increasing the quantity of oat-straw given in combination with clover-hay, the hippuric acid secretion in the urine of sheep was gradually increased; in a similar experiment with barley-straw no such increase took place.

Notwithstanding contradictory appearances, Hofmeister is of opinion that the secretion of hippuric acid is influenced by the protein matters and the fibre of the food, though the necessary conditions can be found only by a closer examination of these substances.

E. Wildt (*Deut. Chem. Ges. Ber.* vi. 1494), fed rabbits with pure grass, and found only a trifling production of hippuric acid; with clover rather more was formed; with meadow grass containing a variety of herbage the production was greatly increased; with *Leontodon Taraxacum* (one of the meadow-plants) the yield was equally large. He concludes that some ingredients of the meadow herbage other than grass or clover are the cause of the formation of hippuric acid.

**HISINGERITE.** A brown amorphous mineral from Lostwithiel in Cornwall has been provisionally described by Church (*Chem. Soc. J.* [2], viii. 3) as hisingerite. Hardness = 2.75. Sp. gr. = 1.74. According to the mean of three analyses, it consists of 52.94 Fe<sup>2+</sup>O<sup>3</sup>, 36.14 SiO<sup>2</sup>, and 10.49 H<sup>2</sup>O (= 99.57), together with 0.82 P<sup>2</sup>O<sup>5</sup> and traces of magnesia. The formula of the mineral is perhaps Fe<sup>2+</sup>O<sup>3</sup>. 2SiO<sup>2</sup> + 2H<sup>2</sup>O, which requires 50.63 p.c. Fe<sup>2+</sup>O<sup>3</sup>, 37.98 SiO<sup>2</sup> and 11.39 H<sup>2</sup>O, the excess of ferric oxide in the analysis being probably due to the difficulty of separating the mineral from the hematitic matrix in which it is imbedded.

**HELMITE.** See TANTALATES.

**HOMOLOGOUS SERIES.** On the Boiling Points of Homologous Organic Compounds, see page 203.

**HOPHITE.** See PHOSPHATES.

**HOPS.** Experiments have been made by A. Muntz (*Compt. rend.* lxxiv. 1044), with the object of ascertaining (1), the nature and quantity of the elements which are removed from the soil by a crop of hops; (2), the proportion in which the various elements are assimilated by the hop-plant during the different phases of its growth.

The following analyses, in which special attention has been bestowed upon the separation of the alkalis, were made with hop-plants gathered on September 17 from a hop-garden at Woerth, at the base of the Liebfrauenberg in Elsass.

## HORNBLLENDE—HUMIC ACID.

*Materials removed from the Soil by a Crop of Hops.*

	2,400 plants grown on 28 acres contain	6,316 plants grown on 1 hectare contain
	kilograms	kilograms
Water . . . . .	4282.560	11270.270
Carbon . . . . .	997.224	2624.861
Hydrogen . . . . .	119.904	315.547
Oxygen . . . . .	764.304	2011.393
Nitrogen . . . . .	34.633	91.141
Phosphoric acid . . . . .	8.625	22.699
Magnesia . . . . .	9.254	24.352
Potash . . . . .	15.888	41.812
Soda . . . . .	0.173	0.455
Mineral matter not determined	50.635	133.278
	6283.200	16535.308

**HORNBLLENDE, and AUGITE.** See AUGITE, p. 117.

**HORTONOLITE.** This name is given by G. J. Brush (*Sill. Am. J.*, [2], xlviii. 17), to a chrysolite containing iron, manganese and magnesium, occurring at Monroe, Orange County, New York, imbedded in calcespar, or in cavities of the same, together with magnetic iron ore. The mineral is yellow to dark yellowish-green, and in the larger masses almost black. The crystals appear black from a coating of another substance. Hardness = 6.5. Sp. gr. = 3.91. Before the blowpipe it becomes black and magnetic, and gives with fluxes the reactions of iron, manganese, and silica. Hydrochloric acid decomposes it completely, with gelatinisation. The mass is always intimately mixed with magnetic iron ore, sometimes also with graphite. The former was removed by the magnet previous to analysis. Two analyses made by W. G. Mixer, gave:

SiO <sub>2</sub>	FeO	MnO	MgO	CaO	K <sub>2</sub> O	Loss by ignition
33.52	44.28	4.72	16.79	trace	0.30	0.26 = 99.87
33.66	44.46	3.98	16.56	trace	0.47	0.26 = 99.39

This composition shows that the mineral is a chrysolite, and the crystallographical and optical examination made by J. M. Blake lead to the same conclusion. The angles are very nearly those of chrysolite, and the occurring faces are  $0P$ ,  $\infty P\infty$ ,  $\infty P_2$ ,  $P\infty$ ,  $P\infty$ ,  $P_2$ ,  $P_4$ . The crystals cleave parallel to the faces of a prism, also parallel to  $0P$ , and perhaps also parallel to  $\infty P\infty$ .

**HUMIC ACID. HUMUS.** W. Detmer (*Landw. Versuchs-Stationen*, xiv. 248) prepares humic acid by exhausting peat and various kinds of peaty soil with solution of potassium carbonate, precipitating the solution with hydrochloric acid, and subjecting the precipitate to a great number of purifying processes. The humic acid was finally precipitated from its solution in boiling water by the addition of hydrochloric acid; it then contained only 0.179 p.c. of nitrogen. The nitrogen present in the earlier stages of purification did not exist as ammonia. The purified humic acid, dried at 120°, gave a mean percentage of 59.75 C., 4.61 H., agreeing with the formula  $C^{50}H^{10}O^8$ ; the composition of the salts shows, however, that the true formula is  $C^{50}H^{10}O^{12}$ .

Humic acid is amorphous. It begins to decompose at 145°. When undried, it dissolves in 8,333 parts of water at 6°, and in 625 parts at 100°; after drying it requires 13,784 parts of boiling water for solution. The presence of salts diminishes its solubility. It is more soluble in phosphoric acid than in other acids. Humic acid reddens litmus; it expels carbonic acid from metallic carbonates, forming insoluble compounds, except with the alkalis. Its solution in ammonia leaves, when dried, a substance having the formula  $C^{50}H^{10}(NH^4)^6O^{12}$ , which is soluble in 2.2 parts of water. Metallic salts form precipitates with ammonium humate. The precipitate formed by calcium chloride has the formula  $C^{50}H^{10}Ca^2(NH^4)^2O^{12}$ ; that by ferric chloride has the formula  $C^{50}H^{10}(Fe^3)^4(NH^4)^2O^{12}$ ; the precipitate by silver nitrate is  $C^{50}H^{10}Ag^6O^{12}$ . All these compounds are amorphous.

The acid prepared from brown peat (called ulmic acid by Mulder) is identical in composition and properties with that obtained from black peat. Humic, the insoluble humus-substance, is difficult to obtain free from undecomposed vegetable fibre. Cranic and apocrenic acids appear to be products of the oxidation of humic acid.



The changes which peat undergoes during its formation are shown by the following analyses of samples from the Nienwalder Moor. The samples were dried at 120°:—

Description of Peat	Ash per cent.	Composition of Organic Substance per cent.			
		N	C	H	O
Brown peat, from surface . . . . .	2.719	0.80	57.75	5.43	36.02
Nearly black peat, at 7 feet . . . . .	7.423	2.10	62.02	5.21	30.67
Black peat, at 14 feet . . . . .	9.164	4.05	61.07	5.01	26.87

The amount of humus in a soil is best ascertained by oxidation with potassium bichromate, and estimation of the carbonic acid evolved. A moderate quantity of humus improves soil in many ways. From its dark colour humus is a good absorbent of heat; its specific heat is much above that of soil; it is hygroscopic, and greatly increases the water-holding power of sandy soils; it has the power of absorbing ammonia; by its decomposition it is a source of carbonic acid; and the mechanical condition of most soils is improved by its presence. When, however, humus is present in excessive quantity, it acts injuriously, by deoxidising ferric salts, and in other ways.

Humic acid is a strictly colloïd body, and cannot, therefore, directly serve for the nourishment of plants. This result is confirmed by experiments with the spores of an alga, *Euglena viridis*, which show that neither humic acid nor neutral ammonium humate is absorbed by this plant from its solutions. Crenic acid is capable of diffusion through membranes; in an experiment with recently germinated peas it was found, by microscopical observation, that crenic acid had passed into the plant from its solution. The oxidation products of humic acid appear, therefore, to be taken up by plants (Dotmer, *Landw. Versuchs-Stationen*, xv. 284).

From experiments by Bretschneider (*Chem. Ackersmann*, 1871, p. 287), it appears that the presence of humic acid in the soil greatly promotes the absorption of nitrogen from the air. The humic acid contained, when dried at 110°: carbon 60.397, hydrogen 4.502, oxygen 35.034, nitrogen .025, ash .042. The experiments were made in four metal dishes, each 6 inches deep, and exposing a surface of 1 square foot. Each vessel contained 15 kilograms of quartz-sand moistened with 3.55 kilograms of water. One vessel was without humic acid; the others contained respectively 1, 3, and 5 p.c. of the weight of the sand. The vessels were exposed freely to the open air for one year, but sheltered from rain and insects, the evaporated water being from time to time replaced. At the end of the experiment the increase of nitrogen with 1 p.c. humic acid was 0.069 gram, with 3 p.c. humic acid 0.239 gram, and with 5 p.c. humic acid 0.454 gram; or, calculating the results for an acre of surface, the increase was respectively 6.24, 21.72, and 41.14 pounds of nitrogen. It is to be observed that the absorption of nitrogen rises more rapidly than the proportion of humic acid present. The experiments do not show that the nitrogen was absorbed as ammonia.

According to Déhéraïn (*Compt. rend.* lxxiii. 1352) humic acid mixed with solution of potash absorbs from the air 7.2 p.c. nitrogen, and humus from old wood mixed with potash absorbs 3.6 p.c.

A peculiar occurrence of humic acid has been observed by T. Lettenmayer (*Deut. Chem. Ges. Ber.* vii. 408). A piece of rotten beech-wood, which had fallen into a cleft of the tree and thus become protected from moisture, was found to be partially covered with a black, glistening, brittle layer of 1 to 2 millimeters in thickness. This was readily soluble, even in cold water, yielding a brown alkaline solution. Acids produced a precipitate consisting of an organic acid of a brownish-red colour. It was found to contain 53.6 p.c. carbon, 4.9 of hydrogen, and but mere traces of nitrogen. After being dried, the acid was insoluble in water, alcohol, and ether, and dissolved with difficulty in alkalis. The original substance was a mixture of the potassium, sodium, and ammonium salts of the acid.

**HUMITE.** *Chondrodite*.—Elaborate investigations of the crystalline form and chemical composition of this mineral have been made by G. vom Rath.

*Crystalline Form* (Pogg. *Ann. Ergänzungsband*, v. 320-413; *Jahrbuch für Mineralogie*, 1871, 634).—Vom Rath's observations confirm the discovery of Scacchi, that the crystals of this mineral are referrible to a three-fold type (i. 930). The

numerous combination-faces might indeed be all referred to one primary form; and if we select for this form a pyramid of any one of the three groups or types, then all faces occurring on the same crystal, or on crystals of the same group, may be represented by simple indices; but if the same pyramid be chosen as the primary form of the crystals of the other two groups, the numerous combination-forms of these crystals will be represented by very complicated indices, although they stand to one another in very simple relations, as above observed, with respect to the forms belonging to one and the same group. Nevertheless, the difference between the three primary forms to which the crystals of the three groups must be referred, in order that their combinations may be represented by simple numbers, relate to only one axis, that is to say, to the ratio of this axis to the other two, whereas the lengths of these latter bear the same ratios to one another in all the three groups.

*Type I.* Calling the macrodiagonal  $a$ , the brachydiagonal  $b$ , and the principal axis  $c$ , the ratios of the axes are:

$$a : b : c = 1.08028 : 1 : 4.40131.$$

The observed forms are:

Pyramids of the principal series . . . . .	$P, \frac{1}{2}P, \frac{1}{3}P$
Macropyramids . . . . .	$\frac{1}{2}P_2, \frac{1}{3}P_2, \frac{1}{4}P_2, \frac{1}{5}P_2, \frac{1}{6}P_2$
Prisms . . . . .	$\infty P, \infty \frac{1}{2}P, \infty \frac{1}{3}P$
Brachydomes . . . . .	$\frac{1}{2}P_\infty, \frac{1}{3}P_\infty, \frac{1}{4}P_\infty, \frac{1}{5}P_\infty, \frac{1}{6}P_\infty$
Macrodomes . . . . .	$\frac{1}{2}P_\infty, \frac{1}{3}P_\infty, \frac{1}{4}P_\infty$
Pinacoids . . . . .	$OP, \infty \frac{1}{2}P_\infty, \infty \frac{1}{3}P_\infty$

Twins occur: (1) with  $\frac{1}{2}P_\infty$  as contact-plane; (2) with  $\frac{1}{3}P_\infty$ . The crystals of the first type are mostly simple; but there are also very regular twins, and, on the other hand, very irregular triple crystals. Cleavage distinctly basal. Colour white, yellowish-white, honey-yellow, chestnut-brown, brown. With the dichroscope, differences of colour are scarcely perceptible; the same also is the case in the other two types.

*Type II.*  $a : b : c = 1.08028 : 1 : 3.14379$ .—Whilst the crystalline forms of the first type are invariably holohedral, those of the second exhibit a peculiar and remarkable hemihedry, which converts a portion of the pyramids into hemipyramids. In consequence of this, the crystals of the second type acquire an apparent monoclinic development, whilst the axial elements remain rhombic. The observed forms of this type are:

Pyramids of the principal series . . . . .	$P, \frac{1}{2}P$
Macropyramids . . . . .	$2P_2, \frac{3}{2}P_2, \frac{5}{2}P_2, \frac{7}{2}P_2$
Brachypyramids . . . . .	$3P_2, \frac{5}{2}P_2, \frac{7}{2}P_2$
Brachydomes . . . . .	$\frac{1}{2}P_\infty, \frac{3}{2}P_\infty, \frac{5}{2}P_\infty$
Macrodomes . . . . .	$\frac{1}{2}P_\infty, \frac{3}{2}P_\infty$
Pinacoids . . . . .	$OP, \infty \frac{1}{2}P_\infty$

Twins: (1) with  $\frac{1}{2}P_\infty$  as contact-plane; (2) with  $\frac{3}{2}P_\infty$ . Colour light to dark yellow. The crystals of this type are more interesting than those of the other two, on account of the great variety of their forms; but a searching investigation is often required, not only for the determination of their type, but even of their relation to humite in general.

*Type III.*  $a : b : c = 1.08028 : 1 : 5.65883$ .—These numbers, compared with the preceding, show that, with equal secondary axes, the principal axes of the first, second, and third types are to one another as 7 : 5 : 9. This third type includes by far the greatest number of humite crystals; and these crystals are not only the most complicated of the humite species, but likewise the most numerously faced of all known minerals. Hemihedry prevails in this as in the second type; but whereas in the latter the pyramid of the principal series is hemihedrally developed, the corresponding pyramids of the third type are holohedral, and the hemihedry occurs in the macro- and brachy-pyramids. The observed forms are:

Pyramids of the principal series . . . . .	$P, \frac{1}{2}P, \frac{1}{3}P, \frac{1}{4}P$
Macropyramids . . . . .	$2P_2, \frac{3}{2}P_2, \frac{5}{2}P_2, \frac{7}{2}P_2, \frac{9}{2}P_2, \frac{11}{2}P_2, \frac{13}{2}P_2, \frac{15}{2}P_2, \frac{17}{2}P_2, \frac{19}{2}P_2$
Brachypyramids . . . . .	$3P_2, \frac{5}{2}P_2, \frac{7}{2}P_2, \frac{9}{2}P_2, \frac{11}{2}P_2, \frac{13}{2}P_2, \frac{15}{2}P_2, \frac{17}{2}P_2, \frac{19}{2}P_2$
Brachydomes . . . . .	$\frac{1}{2}P_\infty, \frac{3}{2}P_\infty, \frac{5}{2}P_\infty, \frac{7}{2}P_\infty, \frac{9}{2}P_\infty, \frac{11}{2}P_\infty, \frac{13}{2}P_\infty, \frac{15}{2}P_\infty, \frac{17}{2}P_\infty, \frac{19}{2}P_\infty$
Macrodomes . . . . .	$\frac{1}{2}P_\infty, \frac{3}{2}P_\infty, \frac{5}{2}P_\infty$
Pinacoids . . . . .	$OP, \infty \frac{1}{2}P_\infty, \infty \frac{3}{2}P_\infty$

Twins occur with  $\frac{1}{2}\bar{P}\infty$  as contact-plane. The colour is mostly brown of various shades, but also yellow, yellowish-white, and white. The colour appears to afford no criterion for the determination of the type. Humite of the third type has hitherto been seldom found together with the first, and never with the second. Its crystals occur especially in two rock-formations, viz., in granular limestone, or in an aggregate of green augite with mica and subordinate separations of lime.

The number of faces observed in humite, including the three pinacoids, and counting the faces common to two types only once, amounts to 135.

**Chemical Composition** (Vom Rath, *Pogg. Ann.* cxlvii. 246-263).—Rammelsberg (*ibid.* lxxxvi. 404-417), from analyses of chondrodrite from North America and from Pargas, and of the three types of humite, concluded that these three types and chondrodrite are similar compounds of one and the same silicate,  $8\text{MgO} \cdot 3\text{SiO}_2$ , with varying quantities of a fluoride,  $8\text{MgF}^2 \cdot 3\text{SiF}^4$ , which may be regarded as isomorphous with the silicate; further, that an increase in the proportion of fluorine is accompanied by a shortening of one of the axes of the crystal, the other two remaining the same. To the proportion 2 : 3 : 4 of fluorine-atoms in the three types III., I., II., correspond primary forms, in which, with equal bases, the vertical axes are as the numbers 1 :  $\frac{7}{9}$  :  $\frac{5}{9}$  or 9 : 7 : 5 (p. 650).

These results seem to show that the atoms of fluorine possess power of essentially modifying the crystalline form. v. Kokscharow has, however, shown that chondrodrite—which was referred by Rammelsberg to the same series, but contains the highest proportion of fluorine, and should, therefore, have a primary form still more obtuse than type II.—really belongs to that type. If, however, two varieties of humite, containing respectively 9 and 5 p.c. of fluorine, can exhibit the same crystalline form, it follows that the morphotropic power supposed to belong to fluorine cannot be exerted in all cases. To throw further light on this point, and determine whether the chemical composition of each of the three types of humite is constant or not, the following analyses were made:—

A pure specimen of each type having been obtained by very careful selection with the aid of the microscope, it was finely pulverised, dried at  $100^\circ$ – $120^\circ$ , then fused with four times its weight of dry sodium carbonate, and the fused mass continuously boiled in a platinum dish, first with pure water, then with water containing a little ammonium carbonate. The whole of the sodium fluoride was thereby dissolved, the filtrate moreover containing a large quantity of silica and a not inconsiderable quantity of magnesium fluoride. The filtrate was evaporated with repeated addition of ammonium carbonate, and the bulky precipitate, after being well washed with hot water, was united with the residuo of the fused mass. The filtrate, on further addition of ammonium carbonate, deposited a second quantity of silica, which was united with the first, and the small quantity of silica still remaining in solution was separated, as recommended by H. Rose, by means of a solution of zinc oxide in ammonia, the zinc silicate being afterwards decomposed by nitric acid, the liquid evaporated down, and the small quantity of silica contained in it estimated in the usual way. The fluorine was precipitated from the alkaline solution by calcium chloride, and the precipitate containing calcium fluoride and a large excess of carbonate was dried, ignited, and treated with acetic acid, which dissolved the carbonate (mixed with caustic lime) leaving the fluoride as a pasty mass. This was dried on the water-bath in a platinum dish, then treated with hot water, collected on a filter, dried, and ignited, whereby the calcium fluoride was obtained as a white powder. The portion of the original fused mass which was insoluble in water, together with the subsequently separated portions of magnesia and silica, was treated by known methods for the estimation of silica, magnesia, ferrous oxide, lime, and alumina.

Four specimens were examined, three from Vesuvius and one from Sweden.

**Type I., from Vesuvius.**—Light brownish humite mixed with light green mica, the humite predominating. The mass exhibits cavities (druses), some filled with large thin laminae of mica; some with pure or nearly pure crystals of humite; some also contain very small quantities of calc spar. Sp. gr. 3.208 (at  $15^\circ$ ).

**Type IIa., from Vesuvius.**—Light yellow crystalline granules intergrown with light greenish mica, almost silver-white in thin laminae. A small quantity of admixed calc spar, not mechanically separable, was removed by digestion in acetic acid. Sp. gr. 3.125 (at  $13^\circ$ ).

**Type IIb., from Sweden.**—Crystals, often very impure in the interior, and consisting, to as much as one-half, of grains of galena, laminae of green mica, &c. Sp. gr. 3.057.

**Type III., from Vesuvius.**—A block, as large as the first, consisting of predominant

humite having an unusual orange-yellow colour, white calcespar, small quantities of greenish and reddish mica, a little white olivine, and isolated slender needles of apatite. Sp. gr. 3.191 (at 17°).

Two analyses were made of each type. The numbers given in the following table are the higher of the two values obtained in each case, as the mode of analysis is adapted to give results in defect rather than in excess.

	I.	IIa.	IIb.	III.
Silica . . . . .	35.63	34.02	33.96	36.82
Magnesia . . . . .	54.45	59.23	53.51	54.92
Ferrous oxide . . . . .	5.12	1.78	6.83	6.48
Lime . . . . .	0.23	—	—	—
Alumina . . . . .	0.82	0.99	0.72	0.24
Fluorine . . . . .	2.43	2.74	4.24	2.40
	98.68	98.76	99.26	100.86

Deducting from the several totals the quantities of oxygen corresponding with the fluorine, we find the following losses:—Anal. I. = 2.34; IIa. = 2.40; IIb. = 2.52; III. = 1.11; whereas an excess might rather have been expected in each case, corresponding with the weight of oxygen replaced by fluorine. These losses appear to be due to water not driven off at 100°–120°, the temperature at which the specimens were dried previous to analysis. Humite dried at 120° gave off 0.34 p.c. water between 120° and 200°.

The following table gives the elementary composition of the several types, after deduction of the oxygen equivalent to the fluorine:—

	I.	IIa.	IIb.	III.
Silicon . . . . .	16.63	15.88	15.85	17.18
Magnesium . . . . .	32.67	35.54	32.11	32.95
Iron . . . . .	3.98	1.38	5.31	3.07
Calcium . . . . .	0.16	—	—	—
Aluminium . . . . .	0.44	0.53	0.38	0.13
Fluorine . . . . .	2.43	2.74	4.24	2.40
Oxygen . . . . .	41.35	41.54	39.58	43.12
	97.66	97.61	97.47	98.85

If now the iron, calcium, and aluminium be replaced in each case by equivalent quantities of magnesium ( $\text{Al}^2 = \text{Mg}^2$ ), the quantities of magnesium in the three types of humite become:

I.	IIa.	III.
35.04	36.82	34.43;

and dividing these numbers and the quantities of silicon, fluorine, and oxygen by the atomic weights of the respective elements, we find for the relative numbers of atoms of these elements—

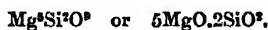
	I.	IIa.	IIb.	III.
Silicon . . . . .	0.594	0.567	0.566	0.613
Magnesium . . . . .	1.460	1.534	1.453	1.435
Fluorine . . . . .	0.128	0.144	0.223	0.126
Oxygen . . . . .	2.584	2.596	2.474	2.695

or, making the number of silicon-atoms = 2, the numbers of the magnesium atoms are:

I.	IIa.	IIb.	III.
5.91	5.41	5.13	4.68

Mean = 5.03.

Hence, neglecting the fluorine, the composition of all humites may be represented by the formula



This formula, which is simpler than the one formerly given by Rammelsberg, viz.  $8\text{MgO}.3\text{SiO}^2$ , may also be deduced from Rammelsberg's own analyses, if they are calculated with the atomic weight of silicon now adopted.

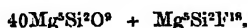
The relative numbers of molecules of the silicate and of the fluoride,  $\text{Mg}^5\text{Si}^2\text{F}^8$ , mixed with it are easily calculated from the relative numbers of atoms of the fluorine and oxygen. For 1 atom of fluorine the preceding values give for the numbers of oxygen-atoms:

I.	IIa.	IIb.	III.
20.1	18.0	11.1	21.4

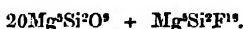
Hence, since each molecule of a fluoride contains twice as many atoms of fluorine as there are atoms of oxygen in the corresponding silicate, it follows that for each molecule of fluoride the numbers of silicate-molecules in the several types are:

$$40.2 \qquad 36 \qquad 22.2 \text{ and } 42.8;$$

and as the differences of fluorine in the three Vesuvian humites scarcely exceed the ordinary errors of analysis, these three humites may be represented by the same formula, viz.:



whereas the Swedish humite contains for the same quantity of fluoride only half that amount of silicate, viz.:



The formula  $\text{Mg}^2\text{Si}^2\text{O}^3$  (two-fifths silicate) may be resolved into that of a hemisilicate (or orthosilicate)  $\text{Mg}^2\text{SiO}^4$  or  $2\text{MgO}.\text{SiO}^2$ , and that of a tritosilicate  $\text{Mg}^2\text{Si}^3\text{O}^5$  or  $3\text{MgO}.\text{SiO}^2$ ; and the fluoride, in like manner, may be regarded as a mixture or combination of  $\text{Mg}^2\text{SiF}^6$  and  $\text{Mg}^2\text{SiF}^{18}$ . The hemisilicate is identical with olivine; the tritosilicate is not known in the separate state. Olivine occurs not unfrequently in very small, nearly colourless crystals, accompanying and intergrown with the humite crystals of Vesuvius.

The general conclusions deducible from the preceding analyses are: (1.) All humites are essentially similar in constitution, and the varying replacement of isomorphous constituents has no decided influence on the types. The variation of colour from the lightest yellow to reddish brown, which is observed in each of the types, shows that the replacement of magnesia by ferrous oxide does not affect the type. Moreover, as the quantities of fluorine in the two varieties of type II. are to one another nearly as 1:2, a similar variation in the amount of fluorine may be predicted in the other two types. (2.) Humites contain a small, but perhaps never altogether failing quantity of alumina, comparable perhaps with the small quantity of that substance occurring in augitic minerals and in the enstatite of the meteorite of Ibbenbürgen. (3.) The variation in the amount of silica (which appears also from Rammelsberg's analyses) shows that the composition of the several types of humite is not absolutely constant.

No other silicate occurring on Vesuvius has hitherto been found to contain fluorine. Fluor-spar, which is of extremely rare occurrence in Vesuvian out-casts, has not been found in association with humite.

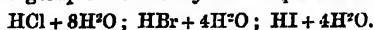
With regard to the occurrence of humite in Vesuvian out-casts, it may be observed that, whereas some Vesuvian minerals occur chiefly or almost exclusively in blocks of one and the same kind, e.g., mejonite chiefly in limestone blocks, sarcolite exclusively in blocks of green augite, humite is found both in limestone and silicate blocks, the two types of mineral aggregates occurring on Vesuvius. Humites are most frequently associated with mica, light green or reddish-yellow, also with green augite, white olivine, black spinel (ceilanite), and calcespar; more rarely with vesuvian and garnet; still more rarely with sanidin, mejonite, and nephelin.

Of the three types of humite, I. appears to be the rarest, and III. the most abundant.

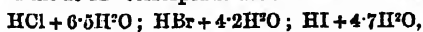
**HYACINTH.** See ZIRCON.

**HYDANTOIC ACID.** See ALLANTOIC ACID, p. 44.

**HYDRACIDS.** 1. *Constitution in Solution and Inverse Reactions.*—Berthelot (*Bull. Soc. Chim.* [2], xix. 386) has investigated the constitution of the liquids resulting from the union of the hydracids with water, by the indications afforded by the heat produced on dilution, the progressive increase of which with the proportion of water shows the existence of a group of definite hydrates represented by the formulæ—



A second method was to observe when a current of carbonic anhydride passed through the solutions ceased to carry off sufficient acid to give any precipitate with silver nitrate. The limit at  $12^\circ$  corresponds with acids of the composition—



agreeing closely with the results of Bineau, and with those obtained by Roscoe (*Chem. Soc. J.* xiii. 166), and by Roscoe & Dittmar (*ibid.* xii. 128). These hydrates, however, do not seem to be definite combinations, as small quantities of acid are carried off by the current of gas even when much more largely diluted. As it appears, from the experiments of Roscoe & Dittmar, that the difference in composition of the hydrated acids boiling at constant temperatures under pressures varying from 0.60 to 2.50 met. does not vary greatly, being from  $\text{HCl} + 6.7\text{H}^2\text{O}$  to  $\text{HCl} + 9.3\text{H}^2\text{O}$ ;  $\text{HBr} + 4.2\text{H}^2\text{O}$  to

$5\text{H}^2\text{O}$ ;  $\text{HI} + 4\cdot7\text{H}^2\text{O}$  to  $5\cdot5\text{H}^2\text{O}$ , Berthelot concludes that they are mixtures of at least two definite hydrates, one of which is stable, whilst the other, the least hydrated, is in a state of partial dissociation varying with the temperature. It is, moreover, the anhydrous acid, and not a definite hydrate, which volatilises below the limit of stability, for hydrobromic acid gas, saturated with the vapour of water, gives the same calorific results on solution as perfectly dry gas.

It would seem, therefore, that concentrated solutions contain a certain amount of anhydrous acid, whose proportion at a given temperature can be calculated, the solutions being mixtures of the hydrates with the anhydrous acid simply dissolved, that is to say, liquefied in them. The precipitation of saturated solutions of the alkaline chlorides by hydrochloric acid also serves to verify the state of hydration of these liquids, the acid taking from the solution of the salt the water necessary to convert it into a stable hydrate. The limit when it ceases to precipitate the salt is  $\text{HCl} + 7\cdot5\text{H}^2\text{O}$  with potassium chloride;  $\text{HCl} + 6\text{H}^2\text{O}$  with sodium chloride,  $\text{HCl} + 9\text{H}^2\text{O}$  with ammonium chloride, and  $\text{HCl} + 9\text{H}^2\text{O}$  with barium chloride, the difference in these results being due principally to the greater or lesser solubility of the salt in hydrochloric acid. The results of these determinations are regarded by Berthelot as sufficient to establish the existence of a certain amount of anhydrous acid in concentrated solutions of the hydracids.

The constitution of the hydracids in solution has an important bearing on chemical reactions, especially those in which the action varies with the concentration of the solution, as for example, in the evolution of sulphuretted hydrogen on treating native antimony sulphide with concentrated hydrochloric acid, and the inverse reaction of the precipitation of sulphide of antimony by sulphuretted hydrogen from a solution of antimony chloride in dilute hydrochloric acid; the neutral point here corresponds, at the ordinary temperature, with an acid of the strength  $\text{HCl} + 6\text{H}^2\text{O}$ . An acid somewhat more concentrated than this attacks native antimony sulphide with disengagement of sulphuretted hydrogen, but on adding a small quantity of water to the liquid, which now contains both antimony chloride and sulphuretted hydrogen in solution, an orange-coloured precipitate of the sulphide immediately makes its appearance. The action of concentrated hydrochloric acid on the antimony sulphide is accompanied by a sensible absorption of heat, due to the formation of the gaseous sulphuretted hydrogen, this absorption being less than the heat of solution of the gas.

In the energetic reducing action exerted by concentrated hydriodic acid, it is really the anhydrous hydracid dissolved which produces the effect 'by virtue of the excess of energy it possesses compared with its definite hydrates,' that is to say the heat corresponding with the transformation of the anhydrous acid contained in the solution into certain stable hydrates. A similar explanation may be given of the inverse action of concentrated hydriodic acid on sulphur, producing sulphuretted hydrogen, and of sulphuretted hydrogen on iodine in presence of a large amount of water, forming hydriodic acid, the neutral point appearing to correspond with an acid of the strength indicated by the formula  $\text{HI} + 7\text{H}^2\text{O}$ , which is the same as for the inverse actions of concentrated sulphuric acid on concentrated hydriodic acid, and of sulphurous anhydride on iodine in presence of water.

Berthelot concludes, therefore, that dilute solutions of the hydracids contain only definite and stable hydrates, whilst concentrated solutions contain at the same time hydrates in a state of dissociation, and also a certain proportion of anhydrous acid. In the phenomena of inverse chemical reactions produced by these two kinds of solutions, it is the anhydrous acid which effects certain reactions, whilst the hydrates are either indifferent or even produce an inverse action.

2. *Reciprocal Displacement of the Hydracids.*—It is well known that the reciprocal displacements of the hydracids are very often the reverse of those exhibited by the corresponding halogen elements. Thus, on the one hand, chlorine displaces bromine, and both expel iodine from its compounds with silver and the alkali-metals, while, on the other hand, hydriodic acid decomposes bromides and chlorides. Berthelot explained these facts some time ago (*Compt. rend.* lxiv. 414), by showing that the reaction which occurs by preference is always the one which evolves most heat. But the calculations having been founded on determinations which more recent experience has rendered doubtful, he has reinvestigated the thermic relations of the halogens and their hydrogen-acids with the metals potassium, silver, and mercury. The result confirms in every way his previous views, with the exception that the heat developed by the reaction of potassium hydrate with the three hydracids is practically the same for each, when the salts produced are the same in solution. But even in this case the heat of formation of the solid salts is in accordance with the general law.

No constant difference appears to exist between the thermic effects either of the halogens or of the hydracids. Thus, whilst with potassium hydrate the three acids evolve identical quantities of heat, the formation of mercuric iodide from the base and

acid disengages 19·2 heat-units more than the formation of the chloride: with silver oxide and hydriodic acid the heat exceeds by 11·2 units that of the corresponding reaction with hydrochloric acid. Similarly the substitution of chlorine for iodine in the mercury salt disengages less heat than in the salt of any other metal. In the case of the alkali-metals, however, and also with certain non-metallic chlorides, &c., an approximation to a constant difference is observed.

Although the heat of formation of the three potassium salts is the same, the acid with a higher equivalent will nevertheless replace one with a lower. This fact may be demonstrated by mixing each of the three hydracids with the potassium salt of the two others in dilute solution, and then evaporating the mixture. An excess of hydriodic acid (2 equivalents) displaces the other two acids, almost completely, and a similar excess of hydrobromic acid as perfectly expels hydrochloric acid; but with single equivalents of the acid and salt, the substitution is incomplete, the residue always containing salts of both acids, that with the higher equivalent, however, preponderating. The numbers furnished by reciprocal reactions are generally nearly the same; and further, although hydrochloric acid is able to expel a small proportion of the other acids, it does so very imperfectly even when in large excess.

These facts admit of the following explanation:—The two hydracids divide the base between them when the solution is dilute, but when during evaporation the point is reached at which a definite hydrate (or rather a system in which the hydrate, the anhydrous acid, and the vapour of water are in a state of equilibrium) begins to pass off, the hydrochloric acid escapes with greatest facility, because in such a system this acid possesses a higher tension of dissociation than the two others at the same temperature (*Compt. rend.* lxxvi. 742); and though the stability of the hydrates of the two latter is very nearly the same, yet the greater volatility of the bromhydric hydrate is the cause of its passing off in preference to the less volatile iodyhydric hydrate. Nevertheless, since the anhydrous acid in both the latter hydrates possesses a certain tension of dissociation, it follows that when the two acids are present in equivalent proportions, or when the more volatile preponderates, a portion of the less volatile will in all cases be lost.

That a division of the base between the two acids actually takes place, may also be demonstrated by adding concentrated hydrochloric acid to a saturated solution of potassium iodide, when a precipitate is obtained consisting of almost pure potassium chloride.

**HYDRACRYLIC ACID,  $C^3H^3O^3$ .** An isomeric of lactic acid obtained by the action of moist silver oxide on  $\beta$ -iodopropionic acid (see LACTIC ACID).

**HYDRARGILLITE.** This mineral occurs (a) in Chester Co., Pennsylvania, as a stalactitic deposit on brown hematite; hardness = 3; sp. gr. = 2·35; (b) at Villarica in Brazil, in spherical lumps of the size of a hazel-nut, cemented together by brown hematite, sometimes radio-fibrous; hardness = 3; sp. gr. = 2·39.

	$Al^2O^3$	$Fe^2O^3$	$H^2O$	$SiO^2$	$P^2O^3$	MgO	FeO
a.	63·84	—	33·45	1·50	0·91	trace	trace = 99·70
b.	63·60	2·00	34·40	—	—	—	= 100

The formula  $Al^2O^3 \cdot 3H^2O$  requires 65·54 p. c.  $Al^2O^3$  and 34·46  $H^2O$  (R. Hermann, *J. pr. Chem.* cvi. 70).

**HYDRASTINE.** An alkaloid occurring, together with berberine, in the rhizome of *Hydrastis Canadensis* or Golden Seal. It crystallises in white shining four-sided prisms, which lose their transparency when dried. It is very bitter and pungent, and provokes in the mouth a feeling of numbness, which causes it to be employed in America as a local anæsthetic. It is nearly insoluble in water, freely soluble in alcohol, ether, chloroform, and benzene. As the last three do not dissolve berberine, the hydrastine may be easily extracted by treating the powdered root in a displacement apparatus with either of these solvents. The proportion so obtained is about 1½ per cent. (*Pharm. J. Trans.* [3], iii. 604).

**HYDRAZOTOLUENE.** See TOLUENE DERIVATIVES.

**HYDRAZULMOXIN,  $C^4N^3H^3O$ .** A compound formed by the action of water on azulmin,  $C^4N^3H^3$ , which is formed by the combination of cyanogen with ammonia (p. 416).

**HYDRISALIZARIN.** See ALIZARIN, p. 40.

**HYDROACRIDINE,  $C^{21}H^{20}N^2$ .** See ACRIDINE, p. 26.

**HYDRO-AMIDO-TETRAZO-RESORUFIN.** See RESORCIN, AZO-DERIVATIVES OF.

**HYDROBENZÖIN.** See BENZOÏN, p. 171.

**HYDROBILIRUBIN.** See BILE-PIGMENTS, p. 100

**HYDROBORO-CALCITE**, more properly called **BORONATRO-CALCITE**. In a commercial sample of this mineral from South America, Graeger (*N. Jahrb. Pharm.* xxxi. 201; *Chem. News*, xx. 119) found—together with 3.76 p.c. NaCl, 1.06 Na<sub>2</sub>SO<sub>4</sub>, and 4.23 residuo, which must be regarded as impurities—the following quantities of the essential constituents:—

CaO	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O
17.03	4.26	52.73	25.98 = 100.00

These proportions may be nearly represented by the formula  $6(\text{CaO} \cdot 2\text{B}_2\text{O}_3) + \text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 + 18\text{H}_2\text{O}$ , which requires 17.85 CaO, 3.29 Na<sub>2</sub>O, 52.07 B<sub>2</sub>O<sub>3</sub> and 26.70 H<sub>2</sub>O.

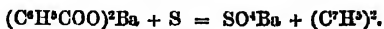
The composition of the mineral is doubtless variable. Rammelsberg, from his own analyses, deduced the formula  $2(\text{CaO} \cdot 2\text{B}_2\text{O}_3) + \text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 + 18\text{H}_2\text{O}$  (1st Suppl. p. 366). Graeger also describes a method of utilising the mineral for the preparation of borax.

**HYDROCARBONS.** *Formation* (F. Pfankuch, *J. pr. Chem.* [2], iv. 35; vii. 97).—Potassium phenate and potassium benzoate yield, when heated together, potassium carbonate and diphenyl. Potassium phenate distilled with potassium acetate yields methylbenzene (toluene); and potassium ethylate distilled with potassium benzoate furnishes ethylbenzene, the yield in both cases being small, in consequence of carbonisation. The addition of pumice or fine sand, and the use of an excess of the acid, increases the product.

The dry distillation of a mixture of potassium phenate and valerate yields isobutylbenzene, boiling at 160°. A mixture of potassium phenate and chlorobenzoate gives monochlorodiphenyl C<sup>6</sup>H<sup>4</sup>Cl melting at 89°. Similarly a mixture of potassium acetate and tribromophenate gives tribromotoluene, C<sup>6</sup>H<sup>3</sup>Br<sub>3</sub>, which crystallises from alcohol in small white needles melting at 150°.

On distilling a mixture of potassium phenate and succinate, a distillate is obtained, yielding, on addition of soda, an oil separable by rectification into toluene and a portion which exhibits a tendency to crystallise and has a very unpleasant smell; its nature has not yet been determined. Potassium phenate and oxalate yield diphenyl, readily obtained pure by washing with soda, then dissolving in alcohol, and precipitating with water. Mononitrodiphenyl is the product of the distillation of a mixture of potassium phenate and nitrobenzoate.

Hydrocarbons are also formed by the action of sulphur on the salts (chiefly barium salts) of organic acids. On heating barium benzoate with sulphur, there is obtained, besides benzene, a crystalline product in considerable quantity, which, under the microscope, is seen to consist principally of two different bodies. The greater portion is toluene, C<sup>6</sup>H<sup>5</sup>, mixed with sulphotoluene. To obtain the toluene pure, the mixed product is either distilled over finely divided lead, obtained from lead acetate by precipitation with zinc, &c., or it is heated in ethereal solution in sealed tubes with lead or copper, and then fractionally distilled. Reaction takes place in the main according to the equation:—



By distilling a mixture of barium acetate and sulphur, and removing the sulphur from the product by means of copper or lead, a liquid hydrocarbon C<sup>6</sup>H<sup>8</sup> (divinyl) is obtained. It is a light oil boiling at about 20°, and having an extremely sharp persistent, but not unpleasant, odour.

*Action of Phosphonium Iodide on Aromatic Hydrocarbons.*—The reducing action of phosphonium iodide, PH<sub>4</sub>I, or phosphine hydriodide PH<sub>3</sub>·HI, is not so powerful as that of hydrogen iodide (1st Suppl. 740). It carries the reduction of hydrocarbons only to the same point as sodium-amalgam does when acting on the acids: consequently, it does not give rise to any compound of the methane series. The stronger reducing power of hydrogen iodide appears to be due to the presence of free iodine, which unites temporarily with the hydrocarbon, and may thus to a certain extent make way for the hydrogen. Now phosphonium iodide is resolved by heat into phosphine and hydrogen iodide, and all the iodine set free by the reducing action is immediately taken up by the phosphine, which is thereby reconverted into phosphonium iodide, with formation of phosphorus iodide.

*Benzene* is not attacked by phosphonium iodide even at 350°. *Toluene* repeatedly and continuously treated with it, finally at 350°, takes up 2 at. hydrogen and is for the most part converted into C<sup>6</sup>H<sup>10</sup>, which boils at 105°–108°. *Xylene* (commercial) is reduced to a hydrocarbon C<sup>6</sup>H<sup>12</sup> which boils at 122°–126°. *Mesitylene* is more easily



reduced than the preceding hydrocarbons; when treated four times with phosphonium iodide, finally at  $280^{\circ}$ , it is almost wholly converted into hexhydromesitylene  $C^9H^{18}$  boiling at  $135^{\circ}$ – $138^{\circ}$ . *Naphthalene* yields an oil boiling at  $170^{\circ}$ – $190^{\circ}$ , and another  $C^{10}H^{12}$  boiling at  $201^{\circ}$ . *Turpentine oil* boiling at  $160^{\circ}$  gives a hydrocarbon  $C^{10}H^{20}$  which likewise boils at  $160^{\circ}$  and is very stable. These results show that the assumption of hydrogen by aromatic hydrocarbons under the influence of phosphonium iodide is related to the number of methyl groups contained in their molecule, 2 at. hydrogen being taken up for each atom of methyl present (A. Baeyer, *Ann. Ch. Pharm.* civ. 266).

*Action of Platinum and Palladium on Hydrocarbons.*—The action of platinum made red-hot and plunged into the vapours of alcohols and ethers, which then keep up the incandescence, appears to extend to all hydrocarbons, volatile oils, bodies similar to aniline, &c., but not to the fixed oils, or sulphuretted essential oils. The products of the imperfect combustion, in every case yet examined, are the aldehyde or acid, or both, analogous to the substance experimented upon. The apparatus employed was modified in different cases, but it consisted essentially of a tube containing the incandescent platinum wire, through which was passed a mixture of air and the vapour, the products being collected in a condenser connected with an aspirator. Toluene treated in this manner yielded bitter almond-oil, which, on exposure to air, was converted into benzoic acid. Marsh-gas did not maintain the incandescence unless the wire was heated by the pile till the action had fairly commenced. Davy found, it is true, that the wire suspended above the flame of his safety-lamp remained red-hot after an explosion of marsh-gas, but this was probably due to the presence of other hydrocarbons. The product of the reaction started by the pile is formic acid; no aldehyde could be obtained. Ethylene-vapour, if allowed to pass very slowly over the platinum, keeps the latter red-hot without an explosion taking place, acetic acid being formed. Many other metals act in the same way as platinum, but on account of their melting when heated in a flame, the experiment is difficult to make. Palladium is a better agent in partial oxidation than even platinum. Marsh-gas keeps it red-hot without the aid of the pile. It is also safer than platinum; no instance occurred of its causing ethylene to explode. Other peculiarities of this metal are that it becomes wrinkled on the surface, is rendered brittle, and diminishes in weight after a few days' use in these experiments (J. A. Coquillon, *Compt. rend.* lxxvii. 444).

**HYDROCOUMARIC ACID.** This term is used in the *First Supplement* (p. 715) as synonymous with melilotic acid,  $C^9H^{10}O^4$ , the acid which exists combined with coumarin in the yellow melilot, and is produced artificially by the action of nascent hydrogen on coumarin. But from more recent experiments by Zwonger (*Ann. Ch. Pharm. Suppl.* viii. 23) it appears that this synthetic process yields two distinct acids, according to the proportion between the nascent hydrogen and the coumarin, viz., monobasic melilotic acid,  $C^9H^{10}O^4$ , when the solution contains only a small quantity of coumarin and the nascent hydrogen is in excess; and bibasic hydrocoumaric acid,  $C^9H^8O^4$ , when the coumarin is in excess.

To prepare hydrocoumaric acid, a concentrated solution of coumarin in strong alcohol is repeatedly treated on the water-bath with thick pasty sodium-amalgam; sodium-hydrocoumarate then separates out, and may be freed from coumarate and melilotate of sodium by boiling with absolute alcohol. The portion of the acid still remaining in the alkaline mother-liquor may be obtained by evaporating off the alcohol, acidulating with acetic acid and precipitating with lead acetate. The precipitate, after repeated boiling with water, is decomposed by hydrogen sulphide, the acid liquid evaporated to the crystallising point, and the acid which separates, purified by conversion into the sodium salt, &c.

Hydrocoumaric acid,  $C^9H^8O^4$ , is slightly soluble in cold, easily in boiling water, and separates therefrom in needles or granular crystals. In ether and in alcohol it is easily soluble. When heated it gives off water at  $100^{\circ}$ , and is converted into its anhydride, hydrocoumarin. It is not altered by sodium-amalgam.

Hydrocoumaric acid is bibasic. Its *ammonium salt* does not crystallise. The *sodium salt*,  $C^9H^6Na_2O^4 + 10H^2O$ , dissolves easily in warm water, and crystallises therefrom in shining colourless tabular prisms: it is dehydrated by alcohol. The *lead salt*  $C^9H^4PbO^4$ , *silver salt*  $C^9H^4AgO^4$ , and *copper salt*  $C^9H^4CuO^4$ , are bulky precipitates, the first two becoming crystalline when left in the liquid.

Hydrocoumarin,  $C^9H^{10}O^4$ , which is best prepared by fusion of hydrocoumaric acid, washing the fused mass with alcohol, and recrystallising from chloroform, is likewise formed, together with melilotic and hydrocoumaric acids, by the action of sodium-amalgam on the aqueous solution of coumarin containing a little alcohol. It forms colourless shining laminae, melts at  $222^{\circ}$ , is decomposed by prolonged fusion.

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It is nearly insoluble in water, alcohol and ether. By boiling with dilute nitric acid, it is converted into a nitro-compound; ammonia and dilute aqueous potash do not act upon it; alcoholic potash converts it into hydrocoumaric acid. It is not converted into mellilotic acid by sodium-amalgam. When fused with potash it yields acetate and salicylate of potassium:  $C^{10}H^{10}O^4 + 6H^2O = 2C^2H^3O^2 + 2C^7H^5O^2 + 3H^2$ .

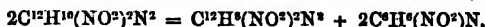
**HYDROCERULIGNONE**,  $C^{14}H^{18}O^6$ . See CERULIGNONE (p. 376).

**HYDROCOTARNINE**. See OPIUM-BASES.

**HYDRODIBROMAZOBENZENE**,  $C^{12}H^{10}Br^2N^2$ . See BENZENE, AZO-DERIVATIVES OF (p. 148).

**HYDRODICHLOORAZOBENZENE**,  $C^{12}H^{10}Cl^2N^2O$ . See BENZENE, AZO-DERIVATIVES OF (p. 151).

**HYDRODINITRAZOBENZENE**,  $C^{12}H^{10}(NO^2)^2N^2$ , is formed by the action of cold ammonium sulphide on dinitrazobenzene, just as hydrazobenzene is formed from azobenzene. It is insoluble in water, and crystallises from boiling alcohol in long yellow needles melting at  $220^\circ$ . Oxidising agents reconvert it into dinitrazobenzene. Heated to  $220^\circ$ – $250^\circ$ , it splits up into dinitrazobenzene and nitraniline, just as hydrazobenzene is decomposed by distillation into azobenzene and aniline (1st Suppl. 272).



The nitraniline thus obtained melts at  $110^\circ$  and is identical with that which is prepared from dinitrobenzene.

By the action of hot ammonium sulphide, hydro-dinitrazobenzene is easily converted into diphenine or hydro-diamido-azobenzene,  $C^{14}H^{10}(NH^2)^2N^2$ , which indeed is formed directly from dinitrazobenzene by the action of hot ammonium sulphide (p. 436) (Lermontoff, *Deut. Chem. Ges. Ber.* v. 236).

**HYDROGEN**. On the Evolution of Hydrogen in Alcoholic Fermentation, see FERMENTATION (p. 517).

*Preparation of Pure Hydrogen Gas.*—Kolbe (*Dingl. polyt. J.* cciv. 160) draws attention to the necessity of using dilute sulphuric acid in the preparation of hydrogen when required in the pure state. He finds indeed that sulphuric, as well as sulphurous, acid can be reduced to hydrogen sulphide by the action of nascent hydrogen, and consequently that hydrogen gas evolved by the action of zinc, even on perfectly pure sulphuric acid, often smells strongly of hydrogen sulphide and blackens lead-paper. The hydrogen sulphide is more abundant, the hotter the acid liquid, and the more concentrated the sulphuric acid which comes in contact with the zinc. If the acid be previously diluted with twice its volume of water, the evolved gas is perfectly free from hydrogen sulphide. Attention to this point is especially necessary in the detection of small quantities of arsenic by Marsh's process, as if the hydrogen contains sulphur, the arsenic may be converted into sulphide and so escape detection.

C. Violette finds that hydrogen, after passing through lead nitrate, silver nitrate, silver sulphate, caustic potash, and oil of vitriol, is perfectly free from hydrocarbons, inasmuch as on passing it over pure copper oxide at red heat, condensing the water in a U-tube, and passing the gaseous products into baryta-water, no opacity is produced in the latter, and the condensed water is quite free from acid reaction.

On the Estimation of Typical Hydrogen in Ammonia-bases, see AMINES (p. 56).

*Combination of Hydrogen with Chlorine in the Absence of Light.*—When charcoal absorbs dry chlorine, the temperature rises, and if dry hydrogen be brought in contact with the charcoal saturated with chlorine, hydrochloric acid is formed in considerable quantity, while at the same time chlorine is given off and the temperature falls (Melsens, *Compt. rend.* lxxvi. 92).

*Absorption of Hydrogen by Palladium.*—Roberts a. Wright (*Chem. Soc. J.* [2]. xi. 112) have endeavoured to determine the state of the hydrogen absorbed by palladium by a comparison between the specific heat of the charged palladium, and that of the palladium in its original state. If the hydrogen, as Graham supposed, enters into the combination as a metal, and the resulting compound is an alloy, then, according to what is known of alloys in general, the specific heat of the charged palladium should be a mean between the specific heats of palladium and of hydrogen in the free state. The experiments show that this is not the case; and that the charged palladium is neither an alloy, nor a mixture of palladium hydride with excess of palladium, but that each several charge must be regarded as giving rise to a distinct compound; and therefore that hydrogen and palladium are capable of combining together in proportions which are not expressible by simple multiples of the combining elements.

Favre, on the other hand (*Compt. rend.* lxxvii. 649), considers palladium charged with hydrogen as a true alloy, because the heat developed by the combination (9,000 gram-degrees) is the same for the last as for the first portion of hydrogen added; whereas the absorption of hydrogen by platinum, and that of other gases by charcoal, are merely cases of capillary affinity, in which the gas may be supposed to form a layer whose density diminishes with increased distance from the surface of the solid; this is indicated by the fact that the later portions of gas absorbed evolve less heat than the earlier. The complete saturation of platinum-black with hydrogen (244 volumes) disengages about 20,700 heat-units for one gram of hydrogen absorbed.

Troost & Hautefeuille (*Compt. rend.* lxxviii. 988) likewise find that palladium forms with hydrogen, a definite compound,  $\text{Pd}^2\text{H}$ , which is further capable of absorbing hydrogen in considerable quantity. The density of the pure compound is 11.06, and that of the melted metal from which it was prepared was 12.0. Supposing, therefore, that the elements unite without condensation, that is to say that the hydrogen in combination with the palladium has the same density that it would have if solidified in the free state, the density of this solidified hydrogen will be 0.62. The same value has been obtained by Dewar (*Phil. Mag.* [4], xlvii. 324), from calculations based upon his own experiments. Graham estimated it at 0.733 (1st *Suppl.* 718), but his calculations appear to have been based on the supposition that the compound of palladium and hydrogen was not of definite constitution.

Troost & Hautefeuille (*Compt. rend.* lxxviii. 807) have also examined the compounds of hydrogen with potassium and sodium. They find that both are definite compounds possessing the metallic lustre, and represented by the formulæ  $\text{K}^2\text{H}$  and  $\text{Na}^2\text{H}$ .

To prepare the potassium-compound, the potassium was placed in a small iron vessel at the bottom of a glass tube; the latter communicated with a manometer, and by means of a three-way tap, with a Sprengel pump, and with a supply of dry hydrogen. No gas was absorbed at temperatures below  $200^\circ$ , but on heating the metal to  $350^\circ$  or  $400^\circ$  absorption proceeded more rapidly. It required, however, 250 hours to saturate 2.5 grams of potassium at a temperature of  $200^\circ$ .

The hydrogenised potassium (potassium hydride) is very brittle at the ordinary temperature, and resembles an amalgam of silver in outward appearance, lustre, and crystalline structure. It can be melted in hydrogen or in a vacuum without undergoing alteration, but if brought into contact with air it takes fire immediately. In a vacuum at about  $200^\circ$ , it begins to decompose, and at  $411^\circ$  the tension of the hydrogen is 760 mm.; in order therefore to saturate potassium at this temperature, it is necessary to heat the metal in an atmosphere of hydrogen the pressure of which is a little above that of the atmosphere. The definite compound absorbs hydrogen in quantities varying with the temperature and pressure; thus at  $300^\circ$  and 760 mm. it dissolves 10 vols. of gas; it is necessary, therefore, in order to obtain the definite combination alone, to expel the gas until the pressure of the hydrogen is no higher than the tension of dissociation for the particular temperature at which the experiment is made.

By extracting the gas with the mercurial pump, it was found that one vol. of potassium was combined with 126 vols. of hydrogen; the formula  $\text{K}^2\text{H}$  requires 124.6 vols.

The sodium-compound is prepared in a manner precisely analogous to that already described. Unlike potassium hydride, it is as soft as sodium at the ordinary temperature, but becomes brittle and easily pulverisable a little before fusion. It is silver-white, and less alterable in the air than the corresponding potassium-compound. The density, taken in naphtha, was 0.959, that of the sodium employed being 0.970; consequently, if the elements are united without condensation, the density of the hydrogen in the compound is 0.63, which is a little higher than that of lithium 0.59. The compound dissolves only small quantities of hydrogen; at  $400^\circ$ , under the atmospheric pressure, it takes up only 3 or 4 times its volume.

Lithium, heated to  $500^\circ$ , under a pressure of 760 mm., absorbs 17 times its volume of hydrogen. Thallium, under similar conditions, dissolves only 3 times its volume.

The hydrogen absorbed by palladium is an active reducing agent. A thin palladium plate covered with palladium black on both sides by means of a battery, and charged with hydrogen, may be kept for weeks in alcohol or ether without losing the hydrogen, excepting that a few bubbles come off at first; but if quickly removed, dried, and wrapped in gun-cotton, it glows in a few seconds, the gun-cotton explodes, and the hydrogen burns for a few seconds with a pale flame. In ether, the gas-bubbles which come off seem to consist partly of ethylene formed by deoxidation. Potassium nitrate is soon reduced to nitrite by the charged palladium (Böttger, *Deut. Chem. Ges. Ber.* vi. 1396).

Seytzeff (*J. pr. Chem.* [2], iv. 418), by passing a mixture of the vapour of benzoyl chloride and hydrogen over heated palladium-black, obtained hydrochloric acid and an

oil apparently consisting of benzoic aldehyde mixed with benzyl alcohol. In a similar manner nitrobenzene may be reduced to aniline.

*Reductio of Silver Nitrate by Hydrogen.*—The precipitation of small quantities of silver by pure hydrogen from solutions of the sulphate, nitrate, and acetate, has been known for some time (1st Suppl. 718), and recently this reaction has been more particularly studied by W. J. Russell (*Chem. Soc. J.* [2], xii. 3). The precipitation takes place with perfectly pure hydrogen, and more readily in a saturated than in a dilute solution. Even from a saturated solution, however, the precipitation occurs only after some time, and the amount precipitated, as compared with that in solution, is always very small. When a saturated solution is used, hydrogen must be bubbled through it for nearly half an hour before precipitation takes place; if the current be continued, a dull greyish substance separates out at first, but afterwards the precipitate is perfectly crystalline and bright, exhibiting a beautiful appearance. At first the amount of silver precipitated is nearly proportional to the time for which it has been exposed to the action of the hydrogen, but after the first 48 hours the amount of silver precipitated increases at a slower and slower rate, and after a certain time the amount of silver present will often begin to diminish. This precipitation of silver by hydrogen is independent of the action of light, but is very much expedited by heat.

On passing hydrogen through the silver nitrate solution only for a minute, and then heating it, a very visible, although not very heavy precipitation immediately appears; it is amorphous, and of a brownish colour. Through a cold solution hydrogen may be passed for about 25 minutes without producing the slightest alteration in appearance. If the solution be then exposed to the air, so that the gas above the liquid diffuses away, silver begins to precipitate after a short time, and a considerable amount will in this way separate out.

The precipitated silver, when examined by the microscope, sometimes exhibits arborescent forms, sometimes appears as a close network of very fine filaments, so intertwined that the whole of the metal can be lifted out of the solution in a connected mass; sometimes it is seen to be in distinct and separate triangular plates of brilliant metal.

The silver prepared by this means is remarkably pure; any gold in the solution would be precipitated with the first portions of silver, and the other metals likely to be present would not be separated out by the hydrogen.

The precipitation may also be effected by merely keeping an atmosphere of the gas above the solution, instead of bubbling it through. If a saturated solution of the silver nitrate be put into a tolerably capacious bottle, and it be then filled with hydrogen, the action will commence rather sooner than if the gas were bubbled through it, and in 18 to 24 hours a somewhat larger amount of silver will be precipitated than by the other process.

The precipitation of the silver, however, cannot be continued indefinitely; indeed, if the solution be left for some time in contact with the atmosphere of hydrogen, the quantity of metallic silver is found to diminish, and, after a few days, yellow crystals of silver nitrite separate out. This result appears to be due in the first instance to the formation of a trace of nitrous acid by the action of the hydrogen on the nitric acid present, this nitrous acid attacking the precipitated silver and combining with it. At the same time nitrogen dioxide is given off, which, by acting on more nitric acid, forms more nitrous acid, thus accelerating the solution of the silver. If much nitric acid be present, the silver nitrite naturally passes back again to nitrate, and this may again be acted upon by the hydrogen. The silver nitrite, on the contrary, is unacted on by hydrogen, and will therefore be the end-product formed by this reaction.

With regard to other metals, *platinum*, *palladium*, and *gold* are completely precipitated from solution by hydrogen in the metallic state, and at ordinary temperatures and pressures. A solution of *copper nitrate*, by long standing in contact with hydrogen, becomes, apparently from the change of colour, converted into nitrite. *Mercuric nitrate* seems to be acted on, and a basic nitrate thrown down, while *bismuth nitrate* seems not to be at all attacked.

**Hydrogen Dioxide,  $H^2O^2$ .** Houszeau (*Compt. rend.* lxx. 519) has demonstrated the existence of this body in snow fallen at Rouen at various times.

The simultaneous formation of *hydrogen dioxide*, *ozone*, and *ammonium nitrite* in the combustion of hydrogen in the air may be shown by burning a small hydrogen flame under a funnel having its neck drawn out to a long tube. The gases issuing from the tube smell strongly of ozone, which may be further identified by means of *china-paper*, &c. The water which condenses is perfectly neutral, and the presence of hydrogen dioxide and ammonium nitrite in it may be demonstrated by the reactions of these compounds with potassium iodide. The formation of these bodies in the combustion

of hydrogen-compounds in the atmosphere may account for their presence in atmospheric deposits (H. Struve, *N. Peters. Acad. Bull.* xv. 325; *Jahresb.* 1870, 199, 209).

**Reactions.**—According to Schönn (*Zeitschr. anal. Chem.* ix. 41, 330) the transient colorations exhibited by certain compounds at high temperatures may be permanently produced by means of hydrogen dioxide. When solid *molybdic acid* or *sodium molybdate* is saturated with hydrated barium dioxide, the mass assumes a faint yellow colour even during the trituration, but on adding an acid, e.g. a few drops of concentrated sulphuric or silicofluoric acid, a deep yellow mass is obtained. *Titanic acid* precipitated by boiling immediately acquires a deep reddish-yellow colour when similarly treated. Solutions of titanic acid are also instantly coloured deep reddish-yellow by a solution of hydrogen dioxide in presence of acids. A solution of molybdic acid or sodium molybdate is turned yellow by an acid solution of hydrogen dioxide, without evolution of gas in either case. On brisk agitation, however, the molybdic acid solution often gives off gas and becomes decolorised. Blue molybdic molybdate is first oxidised and decolorised by hydrogen dioxide, with evolution of gas, but afterwards turns yellow. A solution of titanic acid, which has been turned violet by reducing agents, is coloured deep reddish-yellow by hydrogen dioxide without perceptible previous decoloration. Sodium peroxide reacts with the substances above mentioned in the same manner as barium peroxide. On this account a deep red solution is often obtained in decomposing titanium compounds with sodium. Zinc oxide and stannic oxide do not exhibit any coloration.

Molybdic and titanic acid solutions coloured by hydrogen dioxide become colourless again under the influence of reducing agents such as stannous chloride, zinc-dust, and ferrous oxide. These effects may be explained by supposing either that the coloured substances are merely modifications of the colourless bodies, or, which is perhaps more probable, that the colourless acids take up oxygen from the hydrogen dioxide, and this oxygen, being but loosely combined with them, is easily given up again. A concentrated solution of titanic acid may be used as a test for hydrogen dioxide; it is as delicate as other tests used for the purpose, e.g. reagents containing iodine, and the colour which it gives can only be produced by hydrogen dioxide, not by nitrous acid or other oxidising agents (Schönn).

**Hydrogen Sulphide,  $H^2S$ .** **Formation.**—According to Boillot (*Compt. rend.* lxx. 97) sulphur unites directly with hydrogen under the influence of the electric spark.

**Preparation.**—W. Skay (*Chem. News*, xxvii. 161) proposes to supersede the ordinary laboratory process for the preparation of hydrogen sulphide by the following. The generating flask is charged with fragments of galena and granulated zinc in about equal proportions, and the mixture is covered with dilute hydrochloric acid (1 to 20). An energetic and regular current of sulphuretted hydrogen is then evolved. The gas, accompanied by a little free hydrogen, and requires washing to remove traces of hydrochloric acid.

The apparatus may also be arranged as a simple galvanic couple, in which a piece of massive galena occupies the position of the negative element; the connecting wires are passed through the cork of the apparatus, and are brought into contact with each other by means of binding screws. The evolution of gas commences on making the connection, and ceases instantly when the current is interrupted. This latter arrangement, though somewhat more troublesome to prepare, is nevertheless to be preferred, inasmuch as it avoids the necessity of removing the exciting liquid when the evolution of gas is no longer required.

**Decomposition of the Aqueous Solution.**—Experiments by L. Raab (*N. Rep. Pharm.* xix. 10) show that the decomposition of aqueous hydrogen sulphide is retarded by keeping it in the dark and in a corked bottle, and still more by inverting the bottle and plunging its neck into water.

**HYDROMELLITIC ACID.** See MELLITIC ACID.

**HYDROMUCONIC ACID.** See MUCIC ACID.

**HYDRONAPHTHAQUINONE.** See NAPHTHAQUINONES.

**HYDROPHYRE.** See PEPTONES.

**HYDROPIPERON.** See PIPERONAL.

**HYDROPYROMELLITIC ACID.** See MELLITIC ACID.

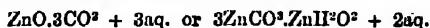
**HYDROQUINONE.** See QUINONE.

**HYDROSANTONIN.** See SANTONIN.



reasons, especially on account of the totally different behaviour of the benzhydroxamates and dibenzhydroxamates: the benzhydroxamates therefore are probably represented by the formula  $C^6H^5O.NH.OM$ .

**HYDROZINCITE.** This mineral, originally found at Bleiberg in Carinthia, and analysed by Smithson in 1803 (called *zinc-bloom* by Rammelsberg, and *zinconise* by Boudant), occurs as a white earthy coating on the deposits of calamine associated with galena in the Argentiera Mine situated in the Commune of Auronzo, in the extreme northern limit of the Cadore. This earthy deposit contains 14.55 p. c.  $CO_2$ , 73.21 ZnO and 11.83  $H^2O$ , answering to the formula:



and not differing greatly in composition from the hydrozincites hitherto examined (i. 798).\*

For the understanding of the formation and decomposition of minerals, it is important to ascertain the intensity of the solvent action exerted upon them by water saturated with carbonic acid. In this respect the carbonates of zinc, native and artificial, exhibit considerable diversities, as the following table will show:—

	Quantity of material dissolved by 1,000 parts by weight of water saturated with $CO_2$ .	Temp.	Pressure
Hydrozincite of Auronzo . . .	0.355	18°	758 mm.
Basic zinc carbonate precipitated in the cold	0.742	17°	759 „
Smithsonite ( $ZnCO_3$ ) from Tarnowitz, in well-defined crystals	0.367	18°	753 „
Smithsonite from Moresnet, perfectly crystallised	0.435	14°	757 „
Stalactitic calamine from Domojovos (Iglesias)	0.850	15°	749 „

Basic zinc carbonate obtained by precipitation, perfectly washed and dried at 100° was found to contain 14.18 p. c.  $CO_2$ , 64.89 ZnO, and 20.15 water. The Smithsonites of Tarnowitz and Moresnet consist of very pure normal zinc carbonate. The calamine of Iglesias gave by analysis—

$H^2O$ and $CO_2$	$SiO_2$	ZnO	FeO	CuO	PbO
12.20	23.07	58.64	3.88	0.45	trace = 98.24.

The solution of this mineral in carbonic acid water contained—besides zinc carbonate-silicic, ferrous oxide, and a trace of copper oxide.

The carbonic solution of the hydrozincite of Auronzo, yielded by spontaneous evaporation a crystalline powder containing 12.98 p. c.  $CO_2$ , 71.25 ZnO, and 15.16  $H^2O$ , which may be represented by the formula  $4ZnO.3CO_2 + 4aq$ , identical with that of the hydrozincite from Bleiberg, analysed by Smithson.

**HYOSCINE**,  $C^6H^{12}N$  (Höhn n. Reichardt, *Ann. Ch. Pharm.* cxlvii. 98). An alkaloid formed, together with hyoscinic acid,  $C^6H^{10}O^2$ , by boiling hyoscyamine with baryta-water:



The boiling must be continued for several hours, the excess of baryta precipitated by carbonic acid, and the liquid evaporated to dryness, mixed with a little water and hydrochloric acid, and exhausted with ether, which dissolves out the hyoscinic acid, leaving the hyoscinic in the acid liquid; and on freeing this liquid from hydrochloric acid by means of silver oxide, evaporating to dryness, dissolving the residue in alcohol, removing traces of baryta by carbonic acid, and again evaporating, the hyoscinic remains as an oily strongly alkaline liquid, having a narcotic odour, and solidifying to a crystalline mass on cooling. The *hydrochloride*,  $C^6H^{12}N.HCl$ , is deliquescent. The *platinchloride* crystallises in beautiful rhombic plates; when boiled with strong potash- or soda-ley, it gives off vapours having a strong alkaline odour.

A small quantity of hyoscinic distils over with the aqueous vapour, together with traces of ammonia, when hyoscyamine is boiled with baryta-water.

**HYOSCINIC ACID**,  $C^6H^{10}O^2$ . This acid, isomeric with phloretic acid, remains on evaporating the ethereal solution obtained in the manner above-described, as a

\* These, according to the analyses given in Rammelsberg's *Mineralchemie* (p. 239), contain from 12.1 to 15.0 p. c.  $CO_2$ , 71.4 to 78.2 ZnO, and 11.2 to 15.1 water. They appear to be mixtures of zinc carbonate and zinc hydrate in various proportions.

strongly acid syrup having a powerful odour like that of benzoic acid, and solidifying over oil of vitriol to long highly lustrous needles. It melts at  $104^{\circ}$ – $105^{\circ}$ , and when cautiously heated sublimates undecomposed, giving off an odour like that of crude benzoic acid. It dissolves very easily in alcohol and ether, also in hot water, but is much less soluble in cold water. The *barium salt*,  $\text{Ba}(\text{C}^{\text{H}}^{\text{H}}\text{O}^{\text{H}})^2 + 2\text{H}_2\text{O}$ , is neutral, and crystallises in nodular tufts of small spicular crystals. A solution of the acid neutralised with ammonia leaves on evaporation an acid mass very much like hyoscinic acid. Lead acetate forms with hyoscinic acid a white precipitate slowly soluble in acetic acid; silver nitrate forms a white flocculent precipitate (Höhn a. Reichardt).

**HYOSCYAMINE**,  $\text{C}^{\text{H}}^{\text{H}}\text{NO}^{\text{H}}$ . This alkaloid has been further examined by Höhn a. Reichardt (*Ann. Ch. Pharm.* cxlvii. 98). To prepare it, 20 pounds of Hungarian henbane-seeds were freed from oil by ether, then exhausted with alcohol of 80 p.c. slightly acidulated with sulphuric acid; the alcohol was distilled off; the resinous masses which separated were collected on a filter; and the aqueous solution, nearly neutralised with soda, was precipitated with tannic acid. The precipitate, dried on earthenware plates, was triturated while moist with slaked lime and exhausted with alcohol; the extract was acidulated with sulphuric acid; the alcohol evaporated, the acid liquid agitated with ether, then made alkaline; and the alkaloid taken up with ether. On evaporating the ether, the hyoscyamine remained as an oily liquid which solidified on standing over sulphuric acid (yield 2.8 grams). The liquid containing the tannic acid still retained a portion of the alkaloid (1.5 grams): it was evaporated, supersaturated with alkali, and exhausted with ether. Lastly an additional 0.3 gram was obtained from the fat oil by agitation with acid, water, &c. Höhn a. Reichardt, however, consider it preferable to neutralise the sulphuric acid extract with lime or potash, evaporate nearly to dryness, supersaturate with lime, and extract with alcohol or ether.

Hyoscyamine forms a thick oily liquid, or in the solid state warty crystalline groups of the colour of white wax; it dilates the pupils very strongly, melts at  $90^{\circ}$ , dissolves easily in alcohol, ether, chloroform, and benzene, and very easily in water. The aqueous solution has a strong alkaline reaction; and in the concentrated state gives precipitates with *alkalis*. With *iodine-water* it forms a crimson-brown, with tannic acid even in very dilute solutions, a white flocculent precipitate; with mercuric chloride a white; with auric chloride a yellowish brown precipitate soluble in excess; with *platonic chloride* a precipitate which cakes together.

Hyoscyamine is resolved by boiling with baryta-water into hyoscinic and hyoscinic acid. The gold-precipitate above-mentioned is decomposed on standing with formation of hyoscinic acid.

Syrupy hyoscyamine appears to form a hydrate, for benzene leaves a portion of it undissolved, and the dissolved portion crystallises more quickly when the benzene is evaporated. On heating the alkaloid, it first emits the characteristic, extremely narcotic odour, then a distinct smell of benzoyl- or salicyl-compounds.

*Hyoscyamine Sulphate*,  $2\text{C}^{\text{H}}^{\text{H}}\text{NO}^{\text{H}} \cdot \text{H}_2\text{SO}^4 + 4\text{H}_2\text{O}$ , crystallises over sulphuric acid, in radiate groups of white shining needles. The *hydrochloride*,  $\text{C}^{\text{H}}^{\text{H}}\text{NO}^{\text{H}} \cdot \text{HCl} + 2\text{H}_2\text{O}$ , crystallises less easily. The *platinochloride*  $2(\text{C}^{\text{H}}^{\text{H}}\text{NO}^{\text{H}} \cdot \text{HCl}) \cdot \text{PtCl}_4$ , forms a resinous precipitate soluble in alcohol.

**HYPOCHLORITE** (A. Frenzel, *Jahrbuch f. Mineralogie*, 1871, 355). The name hypochlorite has been applied to certain varieties of green iron-ore occurring massive or earthy at Schneeberg, Johanngeorgenstadt, and Bräunsdorff, in Saxony. The massive hypochlorite of Schneeberg has a crystallo-granular texture, siskin-green or yellowish-green colour, hardness 6, sp. gr. 2.93–3.0, and even to flat conchoidal fracture. The Bräunsdorff mineral has a siskin-green colour, hardness 6, sp. gr. 2.81. Both have the aspect of hornstone, and pass into the earthy condition, which transformation may sometimes be observed in a lump of the massive mineral. Thin sections of both minerals, when examined by the microscope, exhibit, in the midst of a greenish opaque substance, which forms the principal part, brightly polarising portions (quartz), together with brownish needles arranged in spherical groups. Their composition, according to Frenzel's analyses, is also analogous:—

	$\text{SiO}^2$	$\text{Fe}^2\text{O}^3$	$\text{Sn}^2\text{O}^3$	$\text{Bi}^2\text{O}^3$	$\text{Fe}^2\text{O}^3$
Schneeberg *	88.45	6.00	—	4.76	—
Bräunsdorff	86.00	7.8	5.0	—	trace

These numbers seem to indicate that the hypochlorites in question are mixtures of

\* Schüller analysed the Schneeberg mineral with very different results, viz., 80.24  $\text{SiO}^2$ , 14.98  $\text{FeO}$ , 13.08  $\text{Bi}^2\text{O}^3$ , 10.84  $\text{FeO}$ , and 9.82  $\text{FeO}$  (il. 237).



silicate of bismuth or antimony, with quartz, ferric oxide, and very small quantities of ferric phosphate.

The earthy variety of antimony hypochlorite is similar in constitution to the massive variety. An earthy crust scraped from a lump of the latter, and quite free from foreign admixtures, gave by analysis 78.0 p.c. silica, 11.4 ferric oxide, 7.3 antimonious oxide, and 1.0 water. The earthy bismuth hypochlorite, on the other hand, differs considerably in constitution from the massive. Pure lumps of it, of hardness 1-2, gave 23.08 p.c. silica, 33.33 ferric oxide, and 43.26 bismuth-oxide, agreeing nearly with the formula,  $\text{Bi}^2\text{O}^3 \cdot 2\text{Fe}^2\text{O}^3 \cdot 4\text{SiO}^2$ , or perhaps  $\text{Bi}^2\text{O}^3 \cdot \text{SiO}^2 + 2\text{Fe}^2\text{O}^3 \cdot 3\text{SiO}^2$ , which requires 23.44 p.c. silica, 31.25 ferric oxide, and 45.31 bismuth oxide.

The lump from which this analysis was made exhibited a crystalline structure when broken, and cavities in it were found to be lined with small, indistinct, apparently monoclinic crystals rather harder than the surrounding parts. As this compound differs entirely from Schüler's hypochlorite, Frenzel designates it by a distinct name, bismutho-ferrite. The hornstone-like mixtures may be provisionally distinguished as bismuth and antimony hypochlorite.

**HYPOPHOSPHITES.** See PHOSPHORUS, OXYGEN-ACIDS OF.

**HYPOSULPHITES.** See SULPHUR, OXYGEN-ACIDS OF.

**HYPOXANTHINE.** Salkowski found hypoxanthine in the bone-marrow of leukaemic patients, but did not decide whether it also occurred normally in that substance. P. Heymann (*Pflüger's Archiv. f. Physiologie*, vi. 194) finds that, on adding silver nitrate to the watery extract of the bone-marrow both of man and of the calf, after removal of other substances, a precipitate is formed which has all the characters of argento-hypoxanthine, and on separation of the silver leaves a substance which, in its chemical and microscopical characters, agrees with hypoxanthine.

*Peculiar behaviour of Argento-hypoxanthine.*—E. Salkowski (*ibid.* 91) finds that when a solution of hypoxanthine to which gelatin has been added, is decomposed by silver nitrate, no precipitate, but only an opalescence of the liquid ensues. The opalescent liquid forms no deposit, even after standing at rest for days or on the application of heat. This property of gelatin is a point to be noticed in testing organic liquids and extracts for hypoxanthine. Neither albumin nor glycogen prevents its precipitation by silver nitrate. Gelatin appears, therefore, to act in some way independent of the mere viscosity of the liquid.

## I.

**ICE.** According to a recent determination by Bunsen (*Pogg. Ann.* cxli. 1) the specific gravity of ice is 0.9164.

**IDOCRASE.** Dumour (*Compt. rend.* lxxiii. 1040) has analysed idocrase (vesuvian) from Norway, occurring in rounded, translucent, yellowish grains distributed through a calcareous matrix. Sp. gr. = 3.44. Harder than felspar; fusible in the blowpipe flame; readily acted on by acids. It contained in 100 parts—

$\text{SiO}^2$	$\text{Al}^2\text{O}^3$	$\text{CaO}$	$\text{FeO}$	$\text{MnO}$	$\text{MgO}$	$\text{H}^2\text{O}$
36.32	16.70	34.86	6.20	1.40	0.73	2.58 = 98.79

agreeing with the formula  $18(\text{CaO} ; \text{FeO} ; \text{MnO}) \cdot 4\text{Al}^2\text{O}^3 \cdot 15\text{SiO}^2$  (v. 098).

**IGASURIC ACID.** According to H. Ludwig (*Arch. Pharm.* [3], ii. 137) this acid (iii. 242) belongs to the class of iron-greening tannins. It was prepared by precipitating an aqueous solution of the alcoholic extract of St. Ignatius' beans with neutral acetate of lead, decomposing the precipitate with hydrogen sulphide, and concentrating the filtrate. It formed a yellowish-brown amorphous mass, the solution of which had a strong acid reaction and a sour astringent taste, and could not be made to crystallise.

The acid did not affect ferrous salts, but caused a dark-green coloration in ferric salts. It rapidly reduced ammoniacal silver-solution, and gave a yellow precipitate with neutral acetate of lead. When neutralised with lime-water, it formed an amorphous greenish-brown lime-salt, which was coloured deep brown by caustic soda, and gave with ferric chloride a green coloration, changing to violet-brown on addition of sodium carbonate.

**IGASURINE.** This name has been given to an alkaloid, said to exist in *Nuxvomica*, and to be obtained from the mother-liquors from which strychnine and brucine have separated; but its separate identity has never been satisfactorily established (iii. 243). To throw further light on the question, Jørgensen (*J. pr. Chem.* [2], iii. 175) endeavoured to prepare a periodide from a preparation said to be igasurine. It was dissolved in dilute hydrochloric acid, and fractionally precipitated by a solution of iodine in potassium iodide. The two precipitates thus obtained were washed with cold water and crystallised from alcohol. In both cases violet-blue crystals were obtained, which had the optical properties and crystalline form of brucine tri-iodide. They gave by analysis 49.1 and 49.05 p.c. iodine, the formula of brucine tri-iodide,  $C^{22}H^{22}N^2O^4.HI^3$ , requiring 49.1 p.c. These results tend to show that the so-called igasurine is nothing but brucine.

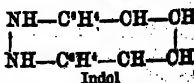
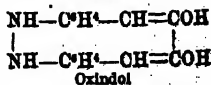
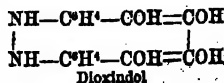
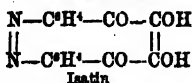
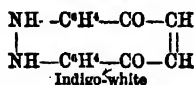
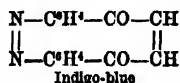
**ELSEMANITE.** Native molybdic molybdate,  $MoO^3.4MoO^3$  from Bleiberg, in Carinthia (see MOLYBDATES).

**INDICAN.** Jaffé finds that, after the subcutaneous injection of indol, very considerable quantities of indican constantly appear in the urine. The elimination of the latter body begins a few hours after injection, and generally ceases within 24 hours. Kuhne has shown that indol is one of the products of the pancreatic digestion, so that Jaffé's previous conjecture that the indican of urine is, partially at least, derived from this source, appears to be verified. The indol of the intestinal canal is, for the most part, ejected with the faeces, imparting thereto its peculiar odour; a small portion is absorbed and reappears in the form of a conjugated compound, indican, in the urine.

**INDIGO.** *Artificial Formation.*—From experiments by Emmerling a. Engler (*Deutsch. Chem. Ges. Ber.* iii. 593), it appears that indigo-blue may be obtained artificially from acetophenone or methyl-phenyl ketone  $C^6H^5.CO.CH^3$ . This ketone treated with nitric acid yields two nitro-derivatives,  $C^6H^5(NO^2)O$ , one solid the other liquid. The solid modification is produced by adding acetophenone to cooled red fuming nitric acid, and separates, on mixing the acid liquid with water, as an oil which solidifies to a crystalline mass on cooling.

The liquid modification, from which indigo is obtained, is produced by the action of nitric acid aided by heat. 70–80 grams of red fuming nitric acid are heated to 46°–50°, and 5–7 grams of acetophenone are then quickly added; and the liquid, which becomes hot, is poured into water as soon as red vapours issue from the flask, whereupon the nitro-compound is obtained as a reddish-yellow syrupy mass. At lower temperatures, the solid modification is formed at the same time, and at higher temperatures, or when the action is too much prolonged, more highly nitrated derivatives are obtained.

To convert the liquid nitro-acetophenone into indigo-blue, it is cautiously heated, in quantities of 5 to 10 grams, till it begins to decompose; the cooled viscid mass is dissolved in chloroform; 40 to 50 times its weight of a reducing agent consisting of 1 pt. soda-lime to 9 pts. zinc-dust is added; and the dried mass is quickly heated in small narrow test-tubes. A dark-coloured sublimate is then formed, which may be driven from one part of the tube to the other, and gives off violet vapours like those of iodine. Emmerling a. Engler did not, however, obtain it in quantity sufficient for analysis, although they repeated the reduction 300 times. They observed, however, that when the sublimate was treated with lime and ferrous sulphate and the clear liquid was exposed to the air, a purple film formed on its surface. From these results they conclude that indigo-blue is the azo-compound of a peculiar ketone, and indigo-white the corresponding hydrazo-compound. They give the following formulae for these and certain allied compounds:



*Formation of Indigo-blue from Isatin.*—Finely pulverised isatin is heated in a sealed glass tube to 75°–80° for several hours with 50 times its weight of a mixture of

parts of phosphorus trichloride and acetyl chloride, with a little free phosphorus. The dark green liquid is then poured into water, and the solution, after filtration, is left for 24 hours in an open dish. The light green liquid gradually turns blue and deposits a dark blue granular powder. This powder is separated by filtration from the clear yellow mother-liquor, and washed with alcohol to remove a red colouring matter soluble therein.

The blue powder thus obtained is insoluble in cold alcohol, dissolves with blue colour in hot alcohol, and in strong sulphuric acid with yellow-green colour, changing to blue on heating; on addition of water a pure blue solution is obtained. The powder volatilises in purple vapours which condense to large needles having a blackish, metallic lustre; it makes a deep blue streak or pure streak on paper, and, in short, it is indigo-blue. The quantity obtained by the process above described is about 10-20 p.c. of the isatin employed. Very small deviations in the mode of operating produce, however, considerable differences in the yield, and sometimes scarcely anything is obtained but a red colouring matter called indigo-purpurin. This substance sublimes more readily than indigo-blue, and condenses to a woolly mass of slender roddish needles; it dissolves in sulphuric acid and the solution diluted with water forms a pure red liquid. It is insoluble in water, slightly soluble in alcohol with deep red colour, dyes silk like fuchsin (Baeyer & Emmerling, *Deut. Chem. Ges. Ber.* iii. 688).

Pure indigo-blue or indigotin, may be obtained in the crystalline state by boiling commercial indigo with *aniline*, whereupon it dissolves, yielding a deep blue solution which, if filtered hot and set aside for some hours, deposits almost the whole of the indigotin in the crystalline state. When required very pure the indigotin should be again crystallised from aniline and the crystals washed with alcohol and dried. As thus obtained it has a fine coppery lustre, equal to that of sublimed indigo. *Benzene*, *chloroform*, boiling *creosote*, and *phenol*, dissolve indigo in small quantity and deposit it, on cooling, in a flocculent state; *alcohol* and *ether*, at their respective boiling points, also dissolve small quantities of indigo (A. de Aguiar and A. Bayer, *Ann. Ch. Pharm.* clvii. 366). Wartha (*Deut. Chem. Ges. Ber.* iv. 334) finds that indigo may also be crystallised from *Venice turpentine*, which, when heated nearly to boiling, dissolves indigo with a fine blue colour, and deposits it on cooling in blue tables; from boiling *paraffin*, which dissolves it with the fine red colour of indigo-vapour, it separates in prisms like those of sublimed indigo. In *petroleum* indigo dissolves with a carmine-red colour; in melted *spermacetic* with a violet, and in *stearic acid* with a blue colour. According to Jacobson (*Diagl. polyt. J.* ccii. 307) indigo likewise dissolves in *nitrobenzene*, *castor oil*, *acetone*, *chloral hydrate*, *camphor*, *oil of turpentine*, *balsam of copaiba*, *cedar oil*, *anilyc alcohol*, *oil of lavender*, *white bees-wax*, *Japanese vegetable wax*, and *Carnauba wax*, the last depositing it in small flaky crystals. A solution of indigo in white wax, heated for some time to its boiling point, passes through several shades of colour, and finally becomes brown, owing to the reduction of the indigo. When powdered indigo is added to melting *picric acid*, deflagration takes place.

*Estimation of Indigo.*—F. Springmühl (*Chem. Cent.* 1870, 703) compares the different methods adopted for the valuation of indigo: 1. The quantity of indigotin may be directly estimated by successive extraction with potash-ley, acetic acid, and alcohol, which dissolve out the indigo-brown, indigo-glutin, and indigo-red, leaving pure indigo-blue. 2. The indigo-blue may be separated from foreign substances by solution in Nordhausen sulphuric acid. The sample is to be dissolved in 20 times its weight of sulphuric acid, the solution diluted with 2,000 parts of water and filtered, and the residue weighed. The sulphuric acid, however, likewise dissolves small quantities of indigo-brown and indigo-red, so that this very simple method gives the amount of indigo-blue rather too high. According to Meyer (*infra*) the sulphuric acid used for dissolving the indigo should have a specific gravity of not less than 1.89.

3. The valuation may be effected by comparing the depth of colour of a solution of the sample with that of a normal solution of indigo. As, however, the normal solution alters by keeping, the results obtained by this method are not very exact. 4. By titration, best with potassium permanganate. A normal solution is prepared by dissolving a known quantity of indigo in sulphuric acid, and the quantity of permanganate required to decolorise it is determined. The sample to be valued is then treated in the same manner and the results compared. Springmühl also recommends titration with acid potassium chromate (iii. 256). According to Meyer, on the other hand, the colour of the resulting isatin-sulphuric acid is so strong that the end of the reaction cannot be distinctly seen, and the results may in consequence be wrong to the amount of  $\frac{1}{4}$  to 1 p.c.

According to Löwenthal (*Zeitschr. anal. Chem.* xi. 45) the method of testing indigo based on the oxidation of the sulphuric acid solution, are not so trustworthy as the estimation of the amount of ash present in the sample; this he finds to vary from 4.5 p.c. in a good sample to 29 p.c.

The quality of indigo is sometimes judged of by its specific gravity. G. Leuchs (*J. pr. Chem.* [2], iv. 349), from the examination of a large number of samples, finds that good indigo, containing 56 to 56.5 p.c. indigotin, has a comparatively low specific gravity (1.34), whilst that of the poorer sorts increases as the proportion of colouring matter becomes smaller, that of a specimen of 27 p.c. being 1.675.

R. E. Meyer (*Dingl. polyt. J.* cxvii. 172) has examined an example of Cochin China indigo and compared its amount of indigotin with that in several kinds of indigo in general use. The following are the results:—

Cochin China Indigo	{52.2 51.5}	mean	51.85 p.c. Indigotin.
Bengal Indigo: (1.) Ordinary, heavy, dark-blue			55.00 "
" " (2.) Gras, (reddish, dark blue).			63.60 "
" " (3.)			68.25 "
" " (4.)			69.50 "
Guatemala Indigo: (1.) Brownish-blue, ordinary			55.25 "
" " (2.) Light blue, ordinary			57.75 "

From this it appears that the Cochin China indigo possesses but a very small colouring power. Its colour is, however, a very fine blue, and it leaves, when dissolved in sulphuric acid, only small quantities of foreign organic matters. The determination of the ash shows that this kind of indigo is richer in inorganic matters than other kinds. Bengal indigo (1.) left 6.63 p.c. ash; Guatemala indigo (1.) left 11.34 p.c., Guatemala (2.) left 2.73 p.c.; whereas Cochin China indigo left 22.36 p.c. ash, consisting chiefly of calcium phosphate with small quantities of calcium carbonate, ferric oxide, alumina, magnesia and soda. By exhausting Cochin China indigo with hydrochloric acid, an excellent product is obtained yielding 74.7 p.c. indigotin, and only 3.74 p.c. ash.

**INDIUM.** *Symbol, In.*—Atomic Weight 113.4 (see 1st Suppl. p. 1137).

*Occurrence.*—Indium has been detected by the spectroscope in zinc-blendes from West Ossipee and Eaton, New Hampshire (U.S.) (H. B. Cornwall, *Chem. News*, xxviii. 28).

*Preparation.*—F. Stolba (*Dingl. polyt. J.* cxviii. 223) prepares indium from indiferous zinc-blende by roasting, as follows: The blende, reduced to a moderately fine powder, is intimately mixed with 10 p.c. of burnt gypsum; the mixture is quickly stirred up with a quantity of water sufficient to make it into a thick paste; this paste is moulded on a paper surface into cakes  $\frac{1}{2}$  to  $\frac{3}{4}$  inch thick, and 4 or 5 inches in diameter; and these cakes, before they have completely hardened, are pierced through their entire thickness with holes 2 lines in diameter at distances of 1 to  $\frac{1}{2}$  inch. The dried cakes are roasted for 4 to 6 hours at a red heat with free access of air, pulverised when cold, treated with hydrochloric or sulphuric acid, and from the resulting solution, kept at the boiling heat in a copper vessel, the indium is precipitated by zinc. From the metallic pulp thus obtained the indium is separated by Böttger's method (1st Suppl. 730).

For the complete and rapid purification of indium from other metals, K. J. Bayer (*Ann. Ch. Pharm.* clviii. 372) employs a method based on the fact that soluble indium compounds are completely precipitated by boiling with acid sodium sulphide, whereas the metals accompanying indium are precipitated by that reagent only partially, and not at all if the solution contains much ammonia-salt. The mode of procedure is as follows:—

Freiberg zinc is dissolved in crude hydrochloric acid, with the exception of a small quantity; the solution is allowed to digest in the cold with this undissolved zinc for 24 to 36 hours, whereby all the indium present is precipitated on the zinc; the clear solution of zinc chloride is then poured off, and the metallic deposit removed from the unattacked zinc. The metallic mud is treated with a few drops of dilute sulphuric acid, to dissolve any basic chloride of zinc, and then washed with hot water until it has no longer an acid reaction. The mixture of metals is then treated with nitric acid; sulphuric acid is added in excess; and the liquid evaporated until all the nitric acid is driven off. By these operations tin is separated as stannic oxide, and lead as sulphate. Water is then added, in which the sulphates of indium, zinc, copper, cadmium, iron, and lead in small quantity, dissolve. The precipitate is removed by filtration, and well washed, and ammonia in great excess is added to the filtrate, whereby the copper, zinc, and cadmium are dissolved, while all the indium and iron remain behind, accompanied by a little zinc, cadmium, lead, and copper. The well-washed precipitate is dissolved in the smallest possible quantity of hydrochloric acid, mixed with acid sodium sulphite in excess, and boiled till the smell of sulphurous acid has almost disappeared. The whole of the indium now separates as a white, fine, crystalline powder, probably

free from copper, zinc, cadmium, and iron. The precipitate is filtered off at once, and washed with hot, de-aerated water. If much iron is present, the precipitate must be filtered in an atmosphere of carbon dioxide; or better, the iron is completely removed by repeated precipitation with sodium bisulphite.

The precipitate may still contain lead or sodium sulphite; it may be obtained pure by dissolving in aqueous sulphurous acid, filtering from any lead sulphite, and boiling the filtrate.

The crystalline indium compound, dried in vacuo over sulphuric acid, has the composition  $2\text{In}^{\text{O}} \cdot 3\text{SO}^2 + 8\text{H}^2\text{O}$ . The insolubility in water of this sulphite renders it suitable for the quantitative estimation of indium. From the sulphite, the various indium salts can be prepared, as it dissolves easily in dilute acids, with evolution of sulphurous oxide.

From a solution of the chloride, the indium can be completely precipitated by boiling with potassium nitrite. The precipitate contains neither nitrous acid nor potassium; it consists of the hydrated oxide  $\text{In}^{\text{O}} \cdot 3\text{H}^2\text{O}$ .

A similar mode of preparing indium from Freiberg zinc is described by Rössler & Wolff (*Dingl. polyt. J.* xciii. 487; *Jahresb.* 1869, 277).

*Indium-ammonium alum*,  $\text{In}^{\text{III}}(\text{NH}_4)(\text{SO}_4)^2 + 12\text{H}^2\text{O}$ , or  $\text{In}^{\text{O}} \cdot (\text{NH}_4)^{\text{O}} \cdot 4\text{SO}_4 + 24\text{H}^2\text{O}$ , is obtained by evaporating over the water-bath solutions of indium and ammonium sulphates, mixed in the proportion of their molecular weights. The concentrated solutions, on standing in the cold, deposit the salt in transparent octohedral crystals.

Indium-ammonium alum crystallises easily in large octohedrons, always exhibiting the cube-faces. It appears to melt at  $36^\circ$ , but really breaks up into a solution of the alum and a salt containing less water (see below). The liquefied mass, when examined with the microscope, is seen to contain monoclinic prisms of the latter salt, whilst octohedral crystals of the alum are again formed as it cools. This breaking up takes place even on triturating crystals of the alum with a pestle, the result being, not a dry powder but a moist pasty mass. The alum is very soluble in water, 1 part of water dissolving 2 parts of alum at  $16^\circ$ , and about 4 parts at  $30^\circ$ . It is insoluble in alcohol. The strongly acid aqueous solution deposits on boiling a white powder, corresponding in composition with alum-stone, and having similar properties.

The formation of the ammonio-indic sulphate with a smaller proportion of water, takes place, as it evidently must do, when a solution of the alum is made to crystallise at  $36^\circ$ . Thus formed, it was found to have the composition represented by the formula  $\text{In}^{\text{III}}(\text{NH}_4)(\text{SO}_4)^2 + 4\text{H}^2\text{O}$ . Corresponding salts were obtained with potassium and sodium sulphates, but it was not found possible to obtain the potassio- and sodio-indic sulphates crystallised with 12 mol. water.

The constitution of the ammonium salt affords additional evidence of the triatomicity of indium (Rössler, *J. pr. Chem.* [2], vii. 14).

**INDOL.** For the constitutional formulæ of this compound, see p. 666.

**INOSITE.** Jacobsen (*Ann. Ch. Pharm.* clvii. 227) has found 0.08 p.c. of this substance in the flesh of a young porpoise, and 0.30 in horse-flesh. According to Hilger (*ibid.* clx. 333) inosite exists abundantly in the juice of the grape. He finds, also, that it ferments in contact with putrid cheese, yielding paralactic acid.

**INDOPHANE.** A blue substance resembling indigo, produced, together with naphthyl-purpuric acid, by the action of potassium cyanide on dinitronaphthol (Hlasiwetz).

According to E. v. Sommaruga (*Chem. Centr.* 1871, 617) the best mode of obtaining it pure is the following:—30 grams of dinitronaphthol with about 2 litres of water are heated to boiling, and sufficient ammonia is added to ensure complete solution. Into this liquid a hot concentrated solution of 45 grams potassium cyanide is dropped. In ten minutes the reaction is completed. The whole is now washed on the filter with boiling water till the filtrate ceases to become coloured. A violet-coloured mass is thus obtained having a beautiful green metallic lustre, and consisting of a mixture of free indophane and a potassium-compound of that body. Washed for a long time with boiling water, the latter becomes coloured, from the solution of a trace of the compound; addition of potassium carbonate prevents this solution, and precipitates from the washings a brown impurity. The mass on the filter is now heated with very dilute hydrochloric acid, filtered, and washed till the filtrate is free from hydrochloric acid.

Pure dry indophane is of a violet colour, and has a beautiful green metallic lustre.

It is insoluble in water, alcohol, ether, benzene, and carbon sulphide, but moderately soluble in sulphuric acid and warm acetic acid, slightly in melted naphthalene. The solutions are purple-red; from these indophane cannot be obtained in the

crystalline state; it may however be sublimed like indigo. Nitric acid appears to oxidise it, forming a brown-red body, soluble in alkaline solutions. Indophane is not reducible by lime and ferrous sulphate, as indigo is.

With aqueous potash or soda indophane yields potassium- and sodium-derivatives which may be obtained pure by filtering and washing till all free alkali is removed; both these compounds greatly resemble indigo. On warming indophane with alcoholic potash-solution, a dark green body is formed at first, and by further action, a humus-like substance is precipitated. Fused potassium hydrate gives the same products with indophane as with naphthyl-purpuric acid.

**INULIN**,  $C^{12}H^{20}O^{10}$ . Schützenberger (*Ann. Ch. Phys.* [4], xxi. 234) has made experiments on the products obtained by the action of acetic anhydride at the boiling heat on dahlia-inulin and elecampane inulin, the results of which agree exactly with those of Ferrouillat a. Savigny (*1st Suppl.* 737) with regard to the composition and the optical rotatory powers of the products. He finds also that dahlia-inulin heated to  $160^{\circ}$  in a sealed tube with 2-3 parts of acetic anhydride is partly dehydrated, and forms two acetyl derivatives; one is soluble in water, and has the rotatory power  $[\alpha] = +55^{\circ}$ , the other is insoluble in water, and has the value  $[\alpha] = +35^{\circ}$ ; both, however, give numbers agreeing with a tetra-acetyl derivative. Saponified with soda, the soluble body gives a resinous mass  $C^{12}H^{16}O^8$ , or inulin mass  $2H^2O$ .

Elecampane-inulin treated in the same manner gave only a black humous mass, together with a trace of dextrorotatory syrup.

**INULOID** (O. Popp, *Ann. Ch. Pharm.* clvi. 190). This is a soluble modification of inulin contained in the bulbs of the Jerusalem artichoke (*Helianthus tuberosus*) and of the dahlia, gathered before they are ripe, or rather at the time when the deposition of inulin in the cells first commences. The expressed juice, after treatment with lead acetate, gives on standing a precipitate resembling starch, and having the composition and most of the properties of inulin, but a lower specific gravity, and a higher degree of solubility. Dried over sulphuric acid it has the composition  $C^{12}H^{20}O^{10} \cdot 2H^2O$ . It gives off its water at  $105^{\circ}$ ; melts at  $130^{\circ}$ - $135^{\circ}$ , passing into an easily soluble state, and decomposes above this point. Its specific rotatory power is  $[\alpha] = -30^{\circ}5'$ ; hence for anhydrous inuloid,  $C^{12}H^{20}O^{10}$ , dried at  $110^{\circ}$  it would be  $-34^{\circ}5'$ , which is very nearly the same in magnitude as that of ordinary inulin. After inversion by acids, the specific rotatory power is  $-79^{\circ}$ . 100 pts. water at  $18^{\circ}$ - $20^{\circ}$  dissolve 1.895 pt. inuloid, and 0.985 pt. inulin. Inuloid dissolves in an ammoniacal solution of copper sulphate, and on boiling is precipitated as a bluish-green substance,  $C^8H^{14}O^4 \cdot CuO$ , which by protracted boiling is resolved into inuloid and copper oxide. It does not reduce alkaline cupric tartrate. After boiling for some time in water, it passes into a soluble gummy mass; by very long heating with water, or more easily with dilute acids at  $110^{\circ}$ - $120^{\circ}$ , it is converted into lævulose; with cold concentrated sulphuric acid it forms a conjugate acid, which is decomposed on dilution; it precipitates the metal from hot ammoniacal copper or silver solutions; is not coloured by aqueous solutions of iodine or bromine; is not precipitated by aqueous solutions of lead acetate or barium hydrate; but on adding to baryta water on the one hand, and to an aqueous solution of inuloid on the other, a quantity of alcohol not sufficient to cause precipitation, and mixing the two alcoholic liquids, a compound of inuloid with baryta is thrown down, which, after moderate washing with water and drying in a vacuum over sulphuric acid, has the composition  $C^8H^{14}O^4 \cdot BaO$ .

Inuloid appears to exist in the plant-juice in the form of a soluble combination with synanthrose. By treatment with lead acetate, a compound of lead and synanthrose is formed, and the inuloid is liberated; or this latter may be set free by causing the juice to ferment at  $10^{\circ}$ - $12^{\circ}$ , by which means the synanthrose is decomposed.

**IODINE**. Sources.—Iodine occurs in considerable abundance in some of the mineral springs of Java. The Genock Watse spring contains in 100 grams, 0.0138 gram of sodium iodide (E. Reichardt, *Arch. Pharm.* [3], ii. 130). The calcium phosphate from the beds in the Departments of Lot and Tarn-et-Garonne contains sufficient iodine to give off violet vapours when treated with sulphuric acid (Kuhlmann, *Compt. rend.* lxxv. 1678). The sodium nitrate of Tarapaca in Peru also contains a considerable quantity of iodine, the mother-liquors of the salt yielding from 2.3 to 4.6 gramm in a litre (E. Wagner, *Dingl. pol. J.* ccv. 76).

**Iodine in Sea-Water**.—According to Sonstadt (*Chem. News*, xxv. 196, 351, 241) iodine exists in sea-water in the form of calcium iodate. That it is not present in the form of an iodide, is shown by the fact that pure sea-water, collected at some distance from land, gives no iodine coloration when acidified and shaken with carbon disulphide but if a very small quantity of solution of sulphurous acid or ferrous sulphate be first added to reduce the iodic acid, and the liquid be subsequently acidified with dilute

sulphuric acid and agitated with carbon sulphide, a recognisable iodine coloration is obtained, even when only 100 c.c. of water are taken. A more exact method of detection is the following:—

200 c.c. of the water are first mixed with a few drops of a slightly alkaline solution of sodium sulphite; 2 or 3 c.c. of a saturated solution of silver acetate are then added; and lastly about one-fourth of the volume of the liquid of strong hydrochloric acid free from chlorine. The liquid is left at rest for a short time, then filtered, and the precipitate washed with dilute hydrochloric acid and distilled water. The filter and precipitate are moistened with a strong solution of caustic soda, and heated in a covered crucible to low redness for a few minutes. After cooling, water is added, the solution filtered, and the filtrate, strongly acidified with dilute sulphuric acid, is shaken up with carbon sulphide and sufficient very dilute chlorine-water to develop the iodine reaction. The presence of iodine is then immediately indicated by the coloration of the carbon sulphide.

Near the shore, however, where sea-water is exposed to the decomposing action of putrifying organic matters, and, in some places, of sewage, the calcium iodate may be reduced to iodide, or it may even contain free iodine. One or two samples taken near the shore were found to give no colour with carbon sulphide when fresh, but after keeping for a few days, the water was found to contain free iodine, and to retain scarcely a trace of the original iodate.

For the quantitative estimation of iodine in sea-water, Sonstadt proceeds as follows: 500 c.c. of the water are treated with a small quantity of arsenious anhydride dissolved in hydrochloric acid; a few milligrams of cupric sulphate are added; the whole is evaporated to dryness; the residue, after gentle heating, is dissolved in the smallest possible quantity of water; and the insoluble cuprous iodide is collected on a filter and washed. The quantity of iodine in it is then determined by igniting the filter with sodium hydrate, and subsequently titrating the acidulated solution of sodium iodide with very dilute chlorine-water and carbon sulphide. Analyses made in this way showed that 250,000 parts of sea-water contain 1 part of calcium iodate, whence it is calculated that a cubic mile of sea-water contains 17,000 tons of calcium iodate or 11,072 tons of iodine.

*Preparation from Residues.*—F. Beilstein (*Zeitschr. f. Chem.* 1870, 528) recovers iodine from residues containing also bromine or chlorine, by means of the well-known reaction of nitrous acid with a solution of potassium iodide acidulated with sulphuric acid. The residues are evaporated and ignited; the solution obtained by lixiviation is mixed with dilute sulphuric acid, and the iodine precipitated by passing nitrous acid (prepared from 1 pt. of crude starch with 6 pts. of crude nitric acid) into the liquid separated by filtration, washed with cold water, and dried over sulphuric acid. From the filtrate, after warming, to expel the iodine still remaining in solution, the bromine may be separated by means of manganese peroxide. As the nitrogen dioxide formed from the nitrous acid in the precipitation of the iodine is reconverted into nitrous acid on coming in contact with the air, it might be used over again in operating on the large scale. The nitrous acid obtained in the preparation of arsenic acid from arsenious acid (for the manufacture of fuchsine) might also be advantageously used in the process above described.

*Impurities in Commercial Iodine.*—The chlorine may be estimated by quickly transferring the iodine, weighed in a stoppered tube, to a large beaker containing 40 c.c. of a freshly prepared concentrated aqueous solution of sulphurous acid, and as soon as the iodine is dissolved (the solution being filtered if necessary) adding half a litre of boiling water, then ammonia in excess, and silver nitrate. The precipitate is treated in the usual manner. To the filtrate from this precipitate nitric acid is added, and the silver chloride estimated.

The ash is also to be estimated by igniting 5 grams of the sample.

The water may be approximately estimated by bringing 1 gram of the sample into a narrow glass tube graduated into tenths of a cubic centimeter, and adding 20 c.c. carbon sulphide, which dissolves the iodine; the solution now occupies 200 divisions of the tube. The tube being well corked is set aside for 2–3 hours, when the water separates out, floating on the surface of the carbon sulphide. Suppose this layer occupies  $\frac{1}{10}$  c.c.; its weight will be 0.1 gram, and the sample will contain 10 per cent. water. (Wanklyn, *Chem. Soc. J.* [2], x. 1115).

Commercial iodine sometimes contains iodine cyanide distributed through its mass in fine needles. This impurity cannot be removed by sublimation, as too much iodine sublimes with it; but by treating the impure iodine with iron and water, a solution is obtained containing both iodide and cyanide of iron; and when this solution is treated with potassium carbonate, the whole of the cyanogen is precipitated,

and the potassium iodide obtained is free from cyanide (Wittstein, *Dingl. pol. J.* cc. 310).

**Optical Properties.**—Iodine in thin layers, as obtained by spreading and pressing it in the fused state between plates of glass, appears brown-red by transmitted light; a very thin layer transmits only the extreme red of the spectrum. Melted iodine appears to have the same colour. Some of its solutions, e.g. in water, alcohol, and acetic acid, exhibit exactly the colour of solid iodine, whilst other solutions, e.g. in carbon sulphide, stannic chloride, phosphorous chloride, &c., exhibit the colour of iodine-vapour (Schulz-Sellack, *Pogg. Ann.* cxl. 334).

The absorption-spectrum of iodine-vapour has been examined by R. Thalén (*Pogg. Ann.* cxxxix. 503). The absorption affects only the half of the spectrum lying between the red and green; and even when it has reached its maximum and this half has completely disappeared, the violet portion remains quite unaltered: hence the violet colour of iodine-vapour. At a lower degree of absorption the bands form several series mixed together, in each of which they are not equidistant, but separate more widely from one another as the length of the wave increases. Each band may be resolved into a number of very fine lines, arranged in more or less regular groups.

**Reactions, Detection, and Estimation.** Iodine dissolves in concentrated sulphuric, nitric, hydrochloric, phosphoric, acetic, tartaric, and citric acids. Some of it crystallises from its solution in sulphuric or nitric acid on standing. The sulphuric and nitric solutions do not give the blue reaction with starch, even when the starch is in excess and unchanged, and water is added, unless the acid is present in very small quantity only. The hydrochloric solution gives the colour with starch unless large quantities of concentrated acid are present. All the solutions yield the iodine to carbon sulphide. From concentrated aqueous or alcoholic solutions of iodine in potassium iodide, concentrated sulphuric or nitric acid precipitates a portion of the iodine.

In presence of *tannin*, iodine cannot be recognised by the ordinary tests, but it is immediately separated by the addition of a few drops of a neutral solution of *ferrie chloride* at a temperature of 37.5°, and may then be recognised by the starch reaction (Tessier, *Zeitschr. Anal. Chem.* xi. 313).

To test *potassium bromide* for iodine, 0.1 gram of the sample may be dissolved in 10–12 c. c. of a 10 p.c. solution of ammonia, and a drop of silver nitrate added. A turbidity, which does not disappear on agitation, indicates the presence of iodine (H. Hager, *Chem. Centr.* 1872, 617).

In presence of *copper salts*, iodine is separated from its compounds by hydrochloric or hydrobromic acid, iodised starch-paste mixed with a small quantity of cupric sulphate turning blue, either immediately or after a short time, on addition of either of those acids. The same effect is produced by addition of hydrocyanic acid or potassium cyanide (Schönn, *Zeitschr. anal. Chem.* ix. 212).

**Detection of Iodine in the form of Potassium Iodide in Urine** (Pelloggio, *Gazzetta chimica italiana*, ii. 75; Giannetti, *ibid.* 253). Pelloggio, in 1870, published a method of detecting iodine in the state of potassium iodide, by subjecting the liquid under examination to the action of an electric current, after addition of starch-paste and slight acidulation with sulphuric or hydrochloric acid. This method was applied to the detection of iodine in urine by Campani, who found it to be inferior in delicacy to the method of testing by bromine-water with addition of starch or of carbon sulphide (*ibid.* i. 472).

Pelloggio, in the paper above referred to, describes experiments on the detection of iodine, both in normal urine to which potassium iodide had been added, and in the urine of patients to whom potassium iodide had been administered, from which he draws the following conclusions:—

1. That for the detection of iodine in urine, the method with carbon bisulphide and bromine-water is not so delicate as that with bromine-water and starch. Moreover, the former method is not to be depended upon, because it is next to impossible to hit the exact quantity of bromine-water required to develop the red coloration without again destroying it; and lastly, it is incapable of detecting very minute quantities of iodine in urine.

2. That the method with bromine-water and starch, though more delicate than that with carbon sulphide, is inferior to that which consists in the use of starch-paste, hydrochloric acid, and the electric current.

Five cubic centimeters of urine containing 0.05 gram of potassium iodide having been diluted with something more than a five-fold quantity of water, and the liquid being divided into two equal portions, one portion treated with starch-paste and a drop of bromine-water did not give any blue coloration, whereas the other portion mixed



with starch-paste and hydrochloric acid and electrolysed, exhibited a number of slender filaments of iodide of starch.

3. That these reactions are less delicate in iodised urine than in the pure solution of potassium iodide, because the urea contained in the urine interferes with them. Hence the colour disappears on agitation, but reappears on further addition of bromine-water.

The superior delicacy exhibited, according to Pelloggio, by the electrolytic method, is attributed by him to the circumstance that the current likewise acts on the urea in such a manner as to prevent its action on the iodide of starch.

A still more delicate test for iodine in presence of urea is, however, afforded by nitromuriatic acid and starch-paste, the nitromuriatic acid decomposing the urea, with formation of nitrous products, and at the same time furnishing the chlorine required to decompose the potassium iodide. With this reagent a distinct blue colour is produced with three drops of iodised urine containing 0.00016 gram. of potassium iodide, and dissolved in 12 c. c. of water (Pelloggio).

The relative delicacy of these tests has also been examined by Giannetti, who has arrived at results opposite to those of Pelloggio. Operating on 5 c. c. of urine containing 0.05 gram of potassium iodide, and diluted with various quantities of water, he obtains the results given in the following table:—

Experiments	Ratio of urine to water	Urine liquid used in each experiment	Potassium iodide contained in each sample	Reactions	
				With starch-paste and bromine-water	With carbon bisulphide and bromine-water
1. Normal urine . . . 50 c.c. Potassium iodide, 0.05 grm.	—	5 c.c.	gram 0.005	Very deep	Very deep
2. Urine of the first } experiment . . . } 5 c.c.		5 c.c.	0.008333	Deep	Deep
3. Urine of the second } experiment . . . } 5 c.c.	1 : 5	5 c.c.	0.008333	Deep	Deep
4. Urine of the third } experiment . . . } 5 c.c.	1 : 11	5 c.c.	0.0041666	Very plain	Deep
5. Urine of the fourth } experiment . . . } 5 c.c.	1 : 23	5 c.c.	0.0020833	Plain	Very plain
6. Urine of the fifth } experiment . . . } 5 c.c.	1 : 47	5 c.c.	0.0010416	Weak colour	Plain
Distilled water . . . 5 c.c.	1 : 95	5 c.c.	0.0005208	Nothing	{ Very perceptible rose colour

From these experiments it appears that the reaction with bromine-water, with addition either of starch-paste or of carbon bisulphide, is more delicate than the electrolytic method, inasmuch as it gives distinct colorations with the iodised urine, diluted in the one case with 47, and in the other with 95 volumes of water, whereas, according to Pelloggio's statement, the limit of the electrolytic reaction appears to be reached when urine containing the same proportion of potassium iodide is diluted with somewhat more than five times its bulk of water. Moreover, the reaction with bromine and bisulphide of carbon appears to be the most delicate of all.

The following are the conditions most favourable to success in these experiments:—  
The undiluted urine (5 c.c.) containing the potassium iodide in the proportion above-mentioned, requires eight drops of saturated bromine-water to produce the red coloration with carbon bisulphide, and six drops to produce the blue colour with starch-paste; a somewhat larger quantity deepens the colour, a large excess destroys it. By diluting the urine more and more, a point is at length reached (Experiments 5 and 6) when a single drop of the bromine-water is too much, and destroys the reaction; but by diluting the bromine with four or five times its volume of water, and adding the liquid drop by drop, the reaction soon shows itself. Strong agitation interferes with

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the reactions, especially when the proportion of potassium iodide is small; but by gentle agitation fine colorations are obtained; this indeed is an essential condition for obtaining a delicate reaction with bromine and bisulphide of carbon.

When the experiment is made with undiluted urine, a considerable quantity of bromine-water is required to obtain the reaction, either with starch-paste or with carbon bisulphide. This fact was observed by Pelloggio, who attributed it to the presence of urea (see above). Giannetti also finds that urea destroys the colour of iodide of starch, but that urine destroys the colour of this compound more quickly than it would be destroyed by the corresponding quantity of pure urea in aqueous solution. Stale urine gradually loses the power of decolorising the iodide of starch. The colour produced by bromine with sulphide of carbon is also destroyed by pure urea and by fresh urine, but not quite so quickly as that of iodide of starch.

Lastly, Giannetti has compared Pelloggio's reaction with nitromuriatic and starch-paste with that obtained by the use of bromine-water and carbon bisulphide, and still finds that the latter is the most delicate test hitherto proposed for the detection of iodides in urine.

*On the Detection of Iodine in Sea-water* (see p. 670).

*Estimation of Iodine in presence of Chlorine and Bromine.*—Potassium iodide is converted by potassium permanganate into free potash and potassium iodate, with separation of manganese dioxide:



As bromide and chloride of potassium are not attacked by the permanganate, this reaction may serve for the estimation of iodine. The solution, which must be slightly alkaline and must contain the chlorine, bromine, and iodine in the state of chloride, bromide, and iodide of an alkali-metal, is heated to boiling, and a solution of 2.5 grams of the permanganate in 497.5 grams of distilled water is added, the liquid being brought to the boiling point after each addition. When the liquid, after repeated boiling, remains distinctly reddish, the excess of permanganate is estimated by titration with sodium thiosulphate, and the iodine is calculated from the quantity of permanganate solution used, each gram of this solution answering to 2 milligrams of iodine (W. Rönige, *Zeitschr. anal. Chem.*, ix. 58). This process slightly modified is applied by E. Sonstadt to the estimation of iodine in Kelp-liquors (*Chem. News*, xxvi. 173; *Chem. Soc. J.* [2], x. 1116).

According to G. M. Donald, on the other hand (*Zeitschr. anal. Chem.*, ix. 377), potassium permanganate cannot be advantageously used for the separation of iodine from bromine and chlorine. He finds that this reagent acts on moderately concentrated solutions of chlorides, bromides and iodides in such a manner as to form a chlorate, bromate, or iodate, with separation of a small quantity of the free halogen. He made use of two solutions of the haloid salts, one containing 1 part of salt in 80 parts of water, the other 1 part of salt in 240 water; also a concentrated solution (1:16) of permanganate, and a very dilute one. In solution of sodium chloride, the strong permanganate solution produces a brown coloration, and after long standing, a precipitate. Dilute solutions remain unaltered even after a day or two. In solution of potassium iodide, concentrated or dilute, the strong permanganate solution produces a brownish precipitate, the odour of iodine being at the same time evolved. The strong solution of potassium bromide likewise gives with the strong permanganate solution, a brown precipitate. A solution of potassium bromide mixed with nitric acid, immediately deposits bromine on addition of permanganate. Dilute solutions of potassium bromide are not altered by the permanganate, the liquid merely becoming coloured by free bromine on addition of a little nitric acid. It would appear then from these experiments that the reactions of the permanganate with moderately strong solutions of the three classes of haloid salts are so very much alike, that this reagent cannot be used as a means of separating iodine from chlorine or bromine.

H. Hübner (*Zeitschr. anal. Chem.*, xi. 397) separates iodine from chlorine and bromine by means of a soluble thallous salt, the separation depending on the fact that thallous iodide,  $TlI$ , is perfectly insoluble in cold water, whereas the corresponding chloride and bromide are soluble. To a cold neutral solution of an alkaline iodide and chloride or bromide, thallous nitrate solution is added drop by drop from a burette, with constant agitation of the liquid, until the precipitate changes in colour from yellow to white. The precipitate is collected, after 8 to 12 hours, in a weighed filter thoroughly washed with water, dried at  $100^\circ$ , and weighed as thallous iodide. To the filtrate silver nitrate is added, and the ensuing precipitate of silver chloride or bromide is collected and weighed as usual. In a well-conducted experiment the error in the quantity of iodine found does not exceed 0.01 p.c.

The separation of iodine from bromine may also be effected by adding to the solution

of alkaline iodide and bromide first a saturated, then gradually a dilute solution of lead nitrate, until the precipitate just begins to change colour from yellow to white. After standing for 12 to 18 hours, the precipitate, which is almost pure lead iodide, is collected on a weighed filter, washed thoroughly, dried at  $110^{\circ}$ , and weighed. The bromide is in the filtrate chiefly as alkaline bromide. Especial care must be taken not to add more lead nitrate than is sufficient to precipitate all the iodide, since if lead bromide is also thrown down, it will be necessary to add a considerable quantity of water to dissolve this bromide, and then the lead iodide will also be partly dissolved. Altogether, this process is not so exact as the preceding.

Iodine and chlorine cannot be separated by the use of lead nitrate.

**Estimation of Iodine, Bromine, and Chlorine by Carius' Method** (i. 47).—Iodide of silver is partially soluble in nitric acid and silver nitrate. The best results are obtained by taking 0.5 to 0.8 gram of iodide,  $1\frac{1}{2}$  equivalent of silver nitrate, 2 c.c. water, and 2 c.c. nitric acid of sp. gr. 1.29. The silver nitrate is dissolved in the water in the tube, and the nitric acid added, whereby much of the nitrate is precipitated in fine crystals; the heating is continued for three hours at  $180^{\circ}$ – $200^{\circ}$ ; and the contents of the tube, after dilution with 200 c.c. of lukewarm water, are boiled for ten minutes. Even with these precautions the percentage of iodine is frequently found to be 0.6 to 1.0 p.c. too small; with bromine and chlorine, the errors are much less (E. Linnemann, *Zeitschr. anal. Chem.* xi. 325).

C. R. A. Wright also finds that a smaller percentage of iodine is obtained if the silver iodide be precipitated in a solution containing much silver nitrate and nitric acid, a higher percentage being obtainable by greatly diluting such a liquid (*Chem. Soc. J.* [2], xi. 527).

**Estimation of Insoluble Iodides.**—The following method is based on the fact that mercuric iodide, lead iodide, silver iodide, and cuprous iodide, dissolve easily even at ordinary temperatures in aqueous sodium thiosulphate (the silver salt less easily than the rest). It is best to take a very small quantity of water, and as little as possible of the sodium salt. On adding ammonium sulphide to the solution, the four metals are completely precipitated, while the whole of the iodine remains in solution. The liquid is evaporated with addition of ammonia, to expel the sulphur as ammonium sulphide, caustic soda is then added and the solid residue is heated in a platinum dish to decompose the salts of polythionic acids. On treating the ignited mass with water, a solution is obtained which quickly reduces ferric chloride, and on mixing it with a large excess of the latter, the whole of the iodine is after a short time set free. The iodine can then be distilled over into a solution of potassium iodide, and estimated in the usual way (E. Meusel, *Deut. Chem. Ges. Ber.* iii. 125).

On the Estimation of Iodine in Sea-water, see p. 671.

**Hydrogen Iodide, or Hydriodic Acid.** The specific gravities of aqueous solutions of hydriodic and hydrobromic acids have been determined by C. R. A. Wright (*Chem. News*, xxiii. 242, 253). The hydriodic acid was prepared by the action of hydrogen sulphide on iodine in presence of water; in the weak acid thus obtained iodine was dissolved; and the solution was digested with phosphorus till its colour disappeared, and finally several times distilled.

The hydrobromic acid was prepared by the action of hydrogen bromide on excess of bromine, and purified by rectification over potassium bromide. The percentages of acid were determined by titration with a normal alkaline solution. The following table gives the values directly obtained:—

Hydriodic Acid		Hydrobromic Acid	
Sp. gr. at $15^{\circ}$	HI per cent.	Sp. gr. at $15^{\circ}$	HBr per cent.
1.708	51.9	1.516*	49.8
1.551	47.2	1.475	48.5
1.442	39.2	1.385	40.8
1.297	30.3	1.248	30.0
1.175	18.5	1.190	23.5
1.053	5.9	1.080	10.4

From these data tables have been constructed by graphic interpolation, showing the densities of the two acids for differences 5 of percentage from 0 to 50; and from these

\* The statement of Löwig (l. 678), that a saturated aqueous solution of hydrobromic acid has a sp. gr. of 1.40, is regarded by Wright as erroneous, the error having probably arisen from the presence of hydrochloric acid in the acid employed.

tables it appears that both in hydriodic and in hydrobromic acid the increase in specific gravity is not proportional to the increase in strength, which is the case with hydrochloric acid, as appears from Ure's table (i. 893). The tables also show that for a given specific gravity, the percentage of HI in the aqueous acid is less than that of HBr, and this again less than that of HCl, thus:

Sp. gr.	Percentage of HCl	Proportionate percentage of HBr	Proportional percentage of HI
1.050	1	0.64	0.54
1.100	1	0.63	0.54
1.150	1	0.62	0.53
1.200	1	0.60	0.52

The specific gravity of hydrobromic acid of given strength is always greater than the mean between those of the corresponding aqueous hydriodic and hydrochloric acids. No simple numerical relation can be traced between the atomic weights of these three acids and the percentages of anhydrous acid contained respectively in the aqueous acids of equal specific gravity.

The specific gravity of aqueous hydriodic acid of different strengths has also been determined by Topsoë (*Zeitschr. für Chem.* [2], vi. 635). The hydriodic acid was prepared by treating 1 part of phosphorus with 19 parts of iodine and 20 parts of water. The specific gravities are those obtained by direct observation at the given temperatures, referred to water at the same temperature as unity. The fourth column of the following table, headed 'Equivalent,' gives the weights of the several aqueous acids containing 1 mol. of HI = 128.

*Specific Gravity of Aqueous Hydriodic Acid.*

Temperature	Specific Gravity	Percentage	Equivalent
12°	1.708	57.74	221.7
13.7	1.706	57.64	222.1
12.5	1.703	57.42	222.0
13	1.696	57.28	223.6
13.7	1.674	56.15	228.0
14	1.630	53.93	237.3
12.5	1.603	52.43	244.2
13	1.5727	50.75	252.2
13.5	1.542	49.13	260.5
13	1.528	48.22	265.5
13	1.4865	45.71	280.0
13	1.451	43.30	295.5
13	1.413	40.45	313.6
13	1.382	38.68	330.9
13	1.347	36.07	354.8
13	1.309	33.07	387.1
13.5	1.274	30.20	423.9
13.5	1.2535	28.41	450.6
13.8	1.225	25.86	494.9
13.8	1.191	22.63	565.6
13.5	1.164	19.97	641.0
13.5	1.126	15.73	813.1
13.5	1.102	13.09	977.6
13	1.095	12.21	1048.3
13.5	1.077	10.15	1261.0
13.5	1.0524	7.019	1823.7
13.5	1.017	2.286	5545.6

Hydriodic acid, after distillation in a stream of carbon dioxide, is nearly colourless, but the stronger solutions quickly decompose and become coloured. The strongest aqueous acid that can be obtained by distillation boils at 127°, and contains 57.74 p.c. HI, which is equivalent to  $\text{HI} + 4.7 \text{ H}^2\text{O}$  (Topsoë). Roscoe found it to contain 57 p.c. (iii. 286).

**Metallic Iodides.** When an iodide mixed with starch-paste is treated with ether, iodine is set free with a blue coloration, at once if concentrated, slowly if

dilute. By filtration and further addition of ether and starch, the iodine can finally be completely removed. The reaction, which applies equally well to natural iodine-waters, but does not affect chlorides and bromides, is probably due to the formation, and subsequent decomposition, of ethyl iodide (E. Ferrière, *Compt. rend.* lxxiv, 1106).

**Periodides.** *Potassium Tri-iodide,  $KI^3$ .*—The solution of iodine in aqueous potassium iodide appears not to contain any definite periodide, inasmuch as when shaken with carbon sulphide it gives up its excess of iodine and becomes colourless (Baudrimont, *Compt. rend.* li. 827). Piffard, indeed (*Zeitschr. Chem. Pharm.* 1861, 151), supposed it to contain a definite periodide, because he found that it gave, with solution of lead acetate, a dark-coloured precipitate which did not give up any excess of iodine to solvents; he regarded this precipitate as  $PbI^3$ , but did not analyse it. Dosios a. Weith, on the other hand (*Zeitschr. f. Chem.* 1869, 379), find that this precipitate gradually gives up its excess of iodine to solvents, and therefore regard it merely as lead iodide,  $PbI_2$ , mixed with free iodine.

A solution of iodine in alcoholic potassium iodide appears, on the other hand, to contain the tri-iodide. Such a solution containing potassium mono-iodide and iodine in proportion to form the tri-iodide, may be agitated with carbon sulphide without colouring the latter, whereas a saturated solution of iodine in carbon sulphide is very easily and completely decolorised by agitation with alcoholic solution of potassium iodide. An aqueous solution of iodine in potassium iodide is decolorised by agitation with mercury, with formation of potassio-mercuric iodide  $KI.HgI^2$ , and separation of mercurous iodide; but an alcoholic solution of potassium tri-iodide shaken with mercury becomes decolorised without yielding a trace of mercurous iodide, the only compound formed being the double iodide above mentioned,  $KI^3 + Hg = KI.HgI^2$  (Jørgensen, *J. pr. Chem.* [2], ii. 347).

**Periodides of Copper and Mercury.**—Cuprous iodide,  $Cu^2I_2$ , is insoluble in water and in alcohol; nevertheless, considerable quantities of it are dissolved when an alcoholic solution of iodine is digested with it for some hours or days at ordinary temperatures, or at a temperature not above  $30^\circ$ . The solution contains nearly 18 atoms of iodine to 1 mol.  $Cu^2I_2$ . At higher temperatures a smaller quantity is dissolved, and after prolonged heating to  $100^\circ$  the solution contains no copper and the cuprous iodide becomes crystalline. From the copper solution mixed with alcohol, water separates nothing, but alcoholic solution of potassium iodide throws down all the cuprous iodide, with formation of potassium tri-iodide. On pouring this liquid, turbid from suspended cuprous iodide, into a large quantity of water, the whole dissolves, the potassium tri-iodide being decomposed, and the higher iodide of copper reproduced.

**Cuprotetrammonium Tetriodide,  $CuI^3.I^3.4NH^3$ .**—When the brown solution of cuprous iodide in alcoholic iodine is heated to  $30^\circ$ , and an alcoholic solution of ammonia heated to the same temperature is added in moderate quantity, there is formed, in the course of a few hours, a brown-black crystalline precipitate, which must be quickly washed with cold alcohol and dried over calcium chloride. The crystals form rhombic tables of  $74^\circ-75^\circ$  and  $106^\circ$ , which appear olive-green in polarised light when the plane of polarisation is parallel to the longer diagonal: dark brown and almost opaque when it is perpendicular thereto. On exposure to the air, they become dull on the surface and give off a small quantity of iodine.

**Cuprotetrammonium Hexiodide,  $CuI^3.I^3.4NH^3$ .**—On mixing a solution of cuprotetrammonium nitrate heated to  $50^\circ$  with a solution of iodine and potassium iodide at the same temperature, and filtering immediately, the filtrate in a few hours deposits a quantity of beautiful brown crystals which, however, must not be dried, but quickly washed with cold water. Under water, in a closed vessel, they may be kept for some time. It is not known whether they contain water, the analysis having been limited to the determination of the proportion between the copper, iodine, and ammonia. The crystals are rectangular plates, often having two opposite angles, or all four, truncated. The rhombus thereby formed has the angles  $76^\circ 30'$  and  $103^\circ 30'$ . They absorb polarised light, but rather feebly, and only when they are of a certain thickness. They are dark brown by transmitted light, or opaque, according as the longer axis of the plate is parallel or perpendicular to the plane of polarisation.

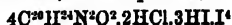
**Cuprotetrammonio-mercurio Iodides.**— $\alpha$ .  $CuI^3.2HgI^2.4NH^3$  is easily obtained by mixing warm solutions of  $KI.2HgI^2$  and sulphate of cuprotetrammonium. As the solution cools, green shining crystals separate, which must be quickly washed with water and dried over calcium chloride in the dark.  $\beta$ .  $CuI^3.HgI^2.4NH^3$ . When the brown crystals of cuprotetrammonium tetriodide are drenched with alcohol and mercury is added to them, they change in a few hours into a blue crystalline mass which, when recrystallised from hot alcoholic ammonia and washed therewith, forms blue shining laminar prisms. The same compound is obtained by mixing a warm solution of

euprotetrammonium sulphate with  $2\text{KI.HgI}^2$ , adding also an excess of potassium iodide, as otherwise the green salt  $\alpha$  is very apt to form.

**Mercury Hexiodide,  $\text{HgI}^6$ ,** is formed when to an alcoholic solution of potassium triiodide warmed to  $50^\circ$ , there is added first an excess of solution of mercuric chloride, then cold water, and the liquid is left at rest for a quarter of an hour. The brown crystalline precipitate which then forms must be washed as quickly as possible with cold water, till the wash-water, after decoloration with sulphurous acid, becomes only a little darker on addition of ammonium sulphide. Even in that case the precipitate retains small quantities of mercuric iodide; indeed, according to Jørgensen, it does not appear possible to obtain the hexiodide quite pure. The crystals are rhombic tables of  $66^\circ$  and  $112^\circ$ – $113^\circ$ , generally having the acute angles truncated; twins are of frequent occurrence. The crystals absorb polarised light and appear light havannah-brown by transmitted light, or perfectly opaque, accordingly as the plane of polarisation is parallel or perpendicular to the shorter diagonal of the rhombus. The compound is decomposed by alcohol, by aqueous potassium iodide, and by prolonged washing with cold water, and gradually loses iodine on exposure to the air (Jørgensen).

**Periodides of Organic Bases.**—These compounds are formed by precipitating the hydrochlorides of the several bases in neutral or acid solution with a solution of iodine in potassium iodide. For the description of the individual compounds, see the several alkaloïds in this volume and in the *First Supplement*.

Of the cinchona bases, the only one which forms a simple tri-iodide is cinchonine, the compound being formed when a neutral alcoholic solution of cinchonine hydriodide is mixed with the calculated quantity of iodine-solution. The other cinchona-bases give black tarry precipitates. Quinine and cinchonine, however, yield periodides containing chlorine as well as iodine. When very dilute solutions of the hydrochlorides of these bases are mixed with about 3 mol. hydrochloric acid and 3 mol. potassium iodide, and left at rest for some time, the compounds,



and



are deposited in brown prisms and laminae. Herapathite may be formed in a similar manner.

The methylic and ethylic derivatives of quinine, quinidine, cinchonine and cinchonidine form crystalline periodides, which have already been noticed (p. 342).

**Triethylphosphonium tri-iodide,  $\text{P}(\text{C}^2\text{H}^5)^3\text{I}^3$ ,** and **Triethylarsonium tri-iodide,  $\text{As}(\text{C}^2\text{H}^5)^3\text{I}^3$ ,** are isomorphous and scarcely distinguishable from one another externally. The periodide of the corresponding antimony-base may be obtained in crystalline form, but is converted by cold water or alcohol into a tarry mass. The *mercury double salts* obtained by agitating the tri-iodides  $\text{N}(\text{C}^2\text{H}^5)^3\text{I}^3$ ,  $\text{P}(\text{C}^2\text{H}^5)^3\text{I}^3$ , and  $\text{As}(\text{C}^2\text{H}^5)^3\text{I}^3$  with metallic mercury are isomorphous. The *bismuth double salts* obtained by mixing the warm alcoholic solutions of the same periodides with solutions of bismuth hydrate in strong hydriodic, hydrobromic, or hydrochloric acid, all crystallise in regular six-sided tables (see p. 192).

**Tetretethylsulphine iodide** forms only a tarry periodide, but crystalline bismuth double salts of it are easily prepared, e.g.  $3\text{S}(\text{C}^2\text{H}^5)^2\text{Br}.3\text{HBr}$ .

For detailed descriptions of all these organic periodides, see Jørgensen (*J. pr. Chem.* [2], ii. 433; iii. 146, 328).

**Iodine Monochloride,  $\text{ICl}$ .**—This compound has been carefully examined by Hannay (*Chem. Soc. J.* [2], xi. 815), who finds that it possesses the same properties, whether it be prepared by passing chlorine over iodine, and distilling the product off iodine to free it from tri-chloride, or by heating iodine with potassium chlorate, and distilling the product off that salt. When recently prepared it remains fluid for several days, but subsequently solidifies. It melts at  $24.7^\circ$ , boils at  $109.5^\circ$ – $101.6^\circ$ , has a specific gravity of 3.263 at  $0^\circ$ , 2.958 at  $98^\circ$ , and expands equally for equal increments of temperature between  $0^\circ$  and  $100^\circ$ . Its vapour-density is 80.27 ( $\text{H} = 1$ ), the formula requiring 81.2.

According to Garnes (*Compt. rend.* lxxiv. 660) iodine monochloride heated to  $40^\circ$  gives off so much vapour that a thickness of 30 c. m. is sufficient to produce an absorption-spectrum. This spectrum consists of 20 fine lines between the extreme red and a point a little beyond the line D, nearly equidistant, and of sensibly equal intensity. No others are observable throughout the spectrum. This system of lines resembles those of the iodine-spectrum more than those of the chlorine-spectrum. It differs, however, from the iodine-spectrum in the absence of lines in the green, and in the fact that the lines of the spectrum of iodine chloride begin sensibly nearer to the red and than do those of the iodine-spectrum.

**Reactions.**—Iodine monochloride acts on the oxygen-acids of chlorine and their salts, with evolution of chlorine and formation of oxygen-acids of iodine, especially iodic acid and its salts. With *hypochlorous acid* the reaction is brisk even at ordinary temperatures; with *chloric acid* it is slow in the cold, energetic at higher temperatures. When chlorine is passed into cooled water containing iodine in suspension till the iodine is completely dissolved, a calculated quantity of solid *potassium chlorate* (1 mol. to 1 at. of iodine dissolved) added to this solution, and the liquid heated, chlorine is evolved and potassium iodate is formed, according to the equation,



Trichloride of iodine acts in the same manner. The expulsion of chlorine by the chlorides of iodine takes place much more easily than with iodine alone. On the other hand, hydrogen iodide and metallic iodides in solution are immediately decomposed by iodine chloride, with liberation of iodine and formation of a chloride (L. Henry, *Deut. Chem. Ges. Ber.* iii. 892).

Iodine monochloride acts on many metals, as potassium, sodium, magnesium, aluminium, copper, mercury, tin, antimony, and bismuth, with various degrees of energy, forming a chloride and iodide of the metal. With *arsenic* it forms arsenious chloride and gives off iodine. *Ordinary phosphorus* treated with iodine chloride bursts into flame, but *amorphous phosphorus* only hisses and emits fumes mixed with iodine-vapour. With *galena* iodine chloride forms chloride of sulphur and iodide of lead. With *sulphur* it reacts feebly, forming iodide and chloride of sulphur. *Selenium* and *tellurium*, especially the latter, act strongly on it, forming chlorides. *Bromine* mixes with iodine chloride in all proportions, without apparent action. Iodine chloride dissolves in *carbon tetrachloride* without action, forming a red solution. When iodine chloride is added to *carbon bisulphide* till saturated, small quantities of white fumes, which smell like sulphur chloride, are evolved, and on treating the product with water, sulphur is precipitated, and a heavy oily body sinks to the bottom, consisting of a mixture of carbon bisulphide, tetrachloride, and sulphochloride. This action of iodine chloride on carbon bisulphide is still more decided on distilling the mixture, when the distillate fumes distinctly, and emits a distinct smell of the sulphochloride while iodine remains in the retort.

On distilling the chloride of iodine from *potassium iodide* several times, it is entirely converted into iodine, while potassium chloride is formed:  $\text{KI} + \text{ICl} = \text{KCl} + \text{I}_2$ . The distillation requires to be repeated several times before the conversion is complete. Iodine chloride acts violently on the *skin*, causing a sharp burning pain, and forming sores difficult to heal (Hannay, *loc. cit.*)

**Iodic and Periodic Acids.** The following determinations of the specific gravities and molecular volumes of these acids have been made by J. Thomsen (*Deut. Chem. Ges. Ber.* vii. 71):—

TABLE I.—*Specific Gravity and Volume of Solution of Iodic Acid at 17° C.*

Number of molecules of water	Specific gravity	Molecular weight	Molecular volume	Increase in volume of the water
$\text{IO}^3\text{H} + 10\text{H}^2\text{O}$ . .	1.6609	356	214.34	34.34
" + 20 " . .	1.3600*	536	392.37	32.37
" + 40 " . .	1.1945	896	750.09	30.09
" + 80 " . .	1.1004	1616	1468.5	28.5
" + 160 " . .	1.0512	3056	2907.2	27.2
" + 320 " . .	1.0258	5936	5786.8	26.8

The last column shows the increase in the volume of water when a molecule of iodic acid is dissolved in it. As the numbers decrease with the increase of water, it follows that contraction takes place when solutions of iodic acid are diluted with water.

Expressing the composition of the iodic acid solution by the formula  $\text{IO}^3\text{H} + a\text{H}^2\text{O}$ , the volume of the solution is expressed by the formula—

$$V_a = 18 \cdot a + 39.1 - \frac{a}{a + 18} \cdot 13.1;$$

\* Compare Kümmerer (p. 593). Thomsen thinks there must be some error in Kümmerer's calculated numbers.

and if the formula holds good for all values of  $a$ , then iodic acid  $\text{IO}^3\text{H}$  in the liquid state will have the volume  $39.1$ . Dividing the molecular weight  $176$  by this number, we find the specific gravity of hydrate of iodic acid in the liquid state to be  $4.50$ . Ditte found it to be  $4.869$  for the crystallised salt at  $0^\circ$  (*Ann. Chim. Phys.* [4], xxi. 22).

The contraction is expressed by  $\frac{a}{a+18} \cdot 13.1$ : it therefore increases with the quantity of water present, and when  $a = \infty$ , that is, on unlimited dilution, it becomes  $13.1$ , or very nearly  $\frac{1}{3}$ rd of the volume of the iodic acid,  $\text{IO}^3\text{H}$ .

TABLE II.—*Specific Gravity and Volume of Solution of Periodic Acid at  $17^\circ \text{C}$ .*

Number of molecules of water	Specific gravity	Molecular weight	Molecular volume	Increase in volume of the water
$\text{IO}^3\text{H}^5 + 20\text{H}^2\text{O}$ . . .	1.4008	588	419.77	59.77
" + 40 " . . .	1.2165	948	779.30	59.30
" + 80 " . . .	1.1121	1068	1409.0	59.29
" + 160 " . . .	1.0570	3108	2940.9	60.2
" + 320 " . . .	1.0288	5988	5820.0	60.0

The last column shows that the volume of water increases by a constant number for each molecule of dissolved acid, and, therefore, that no contraction takes place on solution.

The volume of the solution containing  $\text{IO}^3\text{H}^5 + a\text{H}^2\text{O}$  is therefore—

$$V_a = 18a + 59.6.$$

The specific gravity being equal to the quotient of the molecular weight by the volume, we have accordingly:

$$\begin{aligned} \text{for } \text{IO}^3\text{H} + a\text{H}^2\text{O} \quad & \left\{ \begin{array}{l} \text{Volume} = 18a + 39.1 - \frac{a}{a+18} \cdot 13.1. \\ \text{Specific gravity} = \frac{18a + 176}{18a + 39.1 - \frac{a}{a+18} \cdot 13.1}. \end{array} \right. \\ \text{for } \text{IO}^3\text{H}^5 + a\text{H}^2\text{O} \quad & \left\{ \begin{array}{l} \text{Volume} = 18a + 59.6. \\ \text{Specific gravity} = \frac{18a + 22.8}{18a + 59.6}. \end{array} \right. \end{aligned}$$

These formulæ give the specific gravities of the solutions of the two acids at  $17^\circ$  correct to four decimal places.

**Basicity and Constitution of Iodic Acid.**—The close resemblance exhibited by chlorine, bromine, and iodine, both in the free state and in their combinations with hydrogen, the metals, and many organic bodies, might lead us to expect a similar correspondence in their behaviour to oxygen. In reality, however, iodine differs greatly in this respect from chlorine and bromine.

The composition of the most important oxygen-acids of the three bodies may be expressed by the empirical formula  $\text{RO}^3\text{H}$ ; but the chemical and physical properties of iodic acid are so different from those of chloric and bromic acids that its molecular constitution can scarcely be the same.

(1). Chloric and bromic acids are monobasic, as is shown by the easy solubility of their salts, the non-existence of acid salts, and the impossibility of producing the anhydride directly from the hydrate. Iodic acid, on the contrary, forms salts the greater number of which dissolve with difficulty. It gives with the alkalis chiefly acid salts, and the anhydride can be easily obtained by heat from the hydrate. In all these properties it resembles the polybasic acids.

(2). Iodic acid forms rhombic crystals, and is, in fact, isomorphous with the bibasic succinic and itaconic acids, the constants of the three being—

Itaconic acid . . .	$\alpha$	$\beta$	$\gamma$	Boep.
" . . .	0.581	1	1.255	
Iodic acid . . .	0.590	1	1.231	Schabaz.
" . . .	0.589	1	1.190	
Succinic acid . . .	0.574	1	1.197	



There is only one case of isomorphism between the iodates on the one hand, and the chlorates and bromates on the other, viz., in the case of the barium salt; but the molecules of these salts must, on account of the presence of barium, contain 2 atoms of the haloid element, and will therefore have the same composition,  $R^2O^2Ba$ , whether iodic acid be represented by the ordinary or by the doubled formula.

(3). The relations of affinity, so far as they are exhibited in the heat produced in the formation of the acids of chlorine, bromine, and iodine, show that the last-named element differs from the two former in the constitution of its oxygen-acid.

The following table shows that in the formation of the hydrogen-acids, the heat decreases as the atomic numbers increase, but in the case of the oxygen-acids, while the same rule holds good for chlorine and bromine, iodine shows a remarkable departure from it, the heat evolved in its formation being nearly double of that evolved in the formation of chloric acid:

R	(R,H,Aq)	(R,O <sup>2</sup> H,Aq)
Cl . . . . .	39,320 heat-units.	23,940 heat-units.
Br . . . . .	28,380 "	12,420 "
I . . . . .	13,170 "	55,710 "

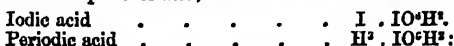
This difference becomes still more striking if the numbers of one of the acid groups are subtracted from those of the other, so as to give the heat of oxidation of the hydrogen-salts into the oxygen-salts—

$$(R,O^2H,Aq) - (R,H,Aq) = (RHAq,O^2).$$

R	(RHAq,O <sup>2</sup> )
Cl . . . . .	-15,380 heat-units.
Br . . . . .	-15,960 "
I . . . . .	+42,540 "

From this it appears that if a solution of hydrochloric or hydrobromic acid could be converted by free oxygen into the corresponding oxygen-acid, there would be in the two cases an equal *absorption* of heat, whereas in the conversion of hydriodic into iodic acid, there is a very considerable *evolution* of heat. It is clear, therefore, that the reactions taking place in the latter case are very different from those which take place in the former, and that the constitution of iodic acid must differ considerably from that of chloric or bromic acid.

(4). If, in accordance with what is above stated, we regard iodic acid as bibasic, and double its usual molecular formula, we obtain one which agrees in a remarkable manner with the formula of periodic acid,  $H^2IO^4$  :—

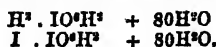


i.e., periodic acid is formed by the substitution of three hydrogen-atoms for one iodine-atom in iodic acid. This substitution is in accordance with the trivalence of iodine in other compounds, the trichloride for example.

This mode of derivation of periodic acid explains the peculiar relations of that acid to bases. Periodic acid, in fact, retains the bibasic character of iodic acid and its normal salts have a constitution represented by that of the sodium salt,  $H^2IO^4Na^2$ . The three atoms of hydrogen which have taken the place of the one atom of hydrogen of iodic acid may, however, be also replaced by metals, giving rise to a large number of so-called basic periodates.

The same view of the constitution of periodic acid agrees with Thomsen's results respecting its heat of neutralisation, inasmuch as the replacement of the first two hydrogen-atoms by sodium gives the normal neutralisation-heat of acids (*Deut. Chem. Ges. Ber.* vi. 2; *Pogg. Ann.* cxl. 90; *Chem. Soc. J.* [2], xi. 595).

The relation between iodic and periodic acid above developed is corroborated by Thomson's investigations on the specific gravities and molecular volumes of their solutions (p. 680). When periodic acid is dissolved in water, the volume of the water increases by 60 c.c. for every molecule of acid dissolved, i.e., for every 228 grams ( $H=1$  gram). If, on the contrary, iodic acid is dissolved in water, the increase in volume of the water is greater for concentrated than for dilute solutions. For every 176 grams of iodic acid ( $=1$  mol.  $IO^2H$ ) there is a variation of from 34 to 27 c.c. if the quantity of water rises by tens up to 320 molecules. The mean value, however, is just half of that of periodic acid, and the two solutions—



have exactly the same volume, viz., 1490.9 and 1500.2, so, that with this quantity of water, a molecule of periodic acid and a double molecule of iodic acid take up exactly the

*same volume.* When more concentrated, the volume of the periodic acid solution is somewhat smaller, when more dilute somewhat larger, than the corresponding solution of iodic acid.

The facts above detailed all tend to the conclusion that iodic acid is bibasic, and that its molecular formula is  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2$ .

*Properties and Reactions of Iodic Acid and Anhydride.*—(A. Ditte, *Ann. Ch. Phys.* [4], xxi. 5.) Iodic anhydride,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2$ , is a white powder, easily soluble in water, insoluble in ether, chloroform, carbon sulphide, and liquid hydrocarbons. Sp. gr. = 4.487 at  $0^\circ$ . Expansion-coefficient, between  $0^\circ$  and  $51^\circ$  = 0.000066. It is a powerful oxidising agent.

Iodic anhydride is commonly said to form two hydrates,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot\text{H}_2\text{O}$  and  $3\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot\text{H}_2\text{O}$ ; but by observations on the tension of the aqueous vapour given off by iodic acid at a determinate temperature (according to the method of Debray and Isambert, 1st *Suppl.* 425, 426) Ditte finds that, however great may be the quantity of anhydride mixed with the monohydrate, the tension at any given temperature is always the same as that of the monohydrate alone: hence it may be inferred that the hydrate  $3\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot\text{H}_2\text{O}$  does not exist.

The monohydrate,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot\text{H}_2\text{O}$ , or *iodic acid*,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2$ , has a specific gravity of 4.629 at  $0^\circ$ : its coefficient of expansion between  $0^\circ$  and  $51^\circ$  is 0.000237. It dissolves easily in water without perceptible alteration of temperature, forming a solution which [? when saturated] boils at  $104^\circ$  under a pressure of 760 mm. and has a specific gravity of 2.842 at  $12.5^\circ$ .

A concentrated solution of iodic acid oxidises common as well as red phosphorus at ordinary temperatures, pulverised arsenic at  $160^\circ$ , sugar-charcoal between  $175^\circ$  and  $180^\circ$ , anthracite at  $210^\circ$ , graphite at  $240^\circ$ , amorphous boron at  $40^\circ$ , crystallised boron at  $200^\circ$ , amorphous and crystallised silicon at  $250^\circ$ , sulphur and selenium at  $150^\circ$ , and acetylene at  $220^\circ$ . Diamond withstands its action even at  $160^\circ$ . Potassium, sodium, magnesium, aluminium, bismuth, zinc, cadmium, iron, copper, mercury, and silver, are attacked by a concentrated solution of iodic acid, some at ordinary temperatures, others when heated; tin, lead, gold, and palladium, are not attacked (Ditte).

According to Thorpe (*Chem. Soc. J.* [2], xi. 548), iodic acid is completely reduced to hydriodic acid, and metallic iodates to iodide by a copper-zinc couple in presence of water, and this mode of reduction may be used for the quantitative analysis of iodates.

Compounds of iodic and sulphuric acid, represented by the formulæ  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot 3\text{SO}^{\text{H}}_2$  and  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot 3(\text{SO}^{\text{H}}_2\cdot 2\text{H}_2\text{O})$ , are described by Millon (*Ann. Chim. Phys.* [3], xii. 330). Ditte, however, did not succeed in preparing either of these compounds. A solution of iodic acid in very strong sulphuric acid prepared at  $310^\circ$  began at  $200^\circ$  to deposit needle-shaped crystals, which, when left for 5 or 6 days on a porous plate under a bell-jar, lost all their adhering sulphuric acid, and were found to contain 5.4 p.c. of that acid, which does not agree with either of Millon's formulæ. The complex compounds of sulphuric acid with the oxides  $\text{IO}^{\text{H}}$  and  $\text{I}^{\text{O}}\text{O}^{\text{H}}$ , described by Millon (iii. 298), as well as these oxides themselves, appear to have no existence. Iodic acid separates unaltered from solution in *nitric acid*, without forming either of the compounds described by Millon and Kämmerer (iii. 209). Neither does iodic acid unite with phosphoric or arsenic acid. Sulphurous, arsenious, sulphydric, hydrochloric, and hydriodic acids are oxidised by it: acetic acid also at  $210^\circ$ - $220^\circ$ . It likewise oxidises oil of turpentine and paraffin.

For Ditte's determinations of the heat of combination and solution of iodic acid, &c., see p. 616.

**Iodates.** *Neutral potassium iodate*,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\text{K}$ , crystallises anhydrous from its aqueous solution at all temperatures. Its specific gravity is 2.801. When it is dissolved in warm dilute sulphuric acid, the hydrated salt,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\text{K}\cdot\text{H}_2\text{O}$ , crystallises out in a few days; but when the salt is heated to  $100^\circ$  with a larger quantity of sulphuric acid diluted with an equal volume of water till the solution begins to crystallise, iodic acid,  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2$ , separates out. From an alkaline solution the neutral iodate crystallises unaltered. The *di-iodate*,  $\text{K}^{\text{O}}\cdot 2\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot\text{H}_2\text{O}$  or  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\text{K}\cdot\text{I}^{\text{O}}\text{O}^{\text{H}}_2$ , is obtained by dissolving the neutral iodate in boiling nitric acid diluted with an equal volume of water, and leaving the solution to cool slowly. The *tri-iodate*,  $\text{K}^{\text{O}}\cdot 3\text{I}^{\text{O}}\text{O}^{\text{H}}_2\cdot 2\text{H}_2\text{O}$  or  $\text{I}^{\text{O}}\text{O}^{\text{H}}_2\text{K}\cdot 2\text{I}^{\text{O}}\text{O}^{\text{H}}_2$ , is formed when the neutral iodate is mixed with a large excess of iodic acid. It gives off all its water between  $160^\circ$  and  $200^\circ$  (Ditte).

According to Sonstadt (*Chem. News*, xxvi. 98) potassium iodate at high temperature is a more powerful oxidising agent than the chlorate or nitrate, inasmuch as its decomposition requires a higher temperature than that of the chlorate, and it gives off pure oxygen, whereas a nitrate when heated gives off a mixture of gases.

When a solution of an alkaline iodate is mixed with an alkaline thiosulphate, no chemical action ensues as long as the solution remains neutral, but the addition of a

small quantity of an acid causes it to become in the first place strongly alkaline; a neutral point is presently reached, after which, if the iodate is in excess, the further addition of acid liberates iodine. The products of the reaction up to neutrality are, a tetrathionate, an iodide, and a salt of the acid used.

When citric or tartaric acid is employed to acidify the mixed solution of iodate and thiosulphate, the solution becomes neutral to test-paper when two molecules of the acid have been added for every six molecules of thiosulphate present, and this neutral point is reached sensibly before iodine is set free. A trisodic salt of the organic acid is formed in both instances. In order to obtain the iodine reaction, a quarter of a molecule more of citric acid and one molecule more of tartaric acid must be added (Sonstadt.)

According to Melsens (*Ann. Chim. Phys.* [4], xxv. 157), potassium iodate is reduced in the animal organism and converted into iodide.

**Calcium Iodate.**—On the existence and quantity of this salt in sea-water, see p. 670. According to Sonstadt (*Chem. News*, xxviii. 397), it is a powerful antiseptic and may be advantageously used for preserving meat, fish, eggs, &c., from putrefaction. The sodium, potassium, and magnesium salts do not act so powerfully in this way as the calcium salt.

**Erbium Iodate**,  $\text{I}^{\text{O}}\text{Eb} + 2\text{H}^{\text{O}}$ , is uncrystallisable (Clève, *Bull. Soc. Chim.* [2], xix. 289).

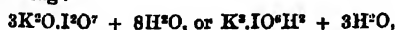
**Glucinum Iodate** remains, on evaporation, as a gummy mass (Atterberg, *ibid.* 497).

**Thallium Iodates.**—**Thallous iodate**,  $\text{TI}^{\text{I}}\text{O}^{\text{O}}$ , is obtained as a white non-crystalline powder by heating thallious hydrate with iodic acid; or by decomposing a thallious salt with a soluble iodate. It is nearly insoluble in water, and dissolves but sparingly in nitric acid: it remains unaltered at  $150^{\circ}$ , but when more strongly heated it melts to a brown liquid, gives off oxygen and iodine, and yields a sublimate of thallious iodide, and a residuo of thallious oxide which strongly attacks glass.

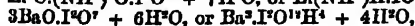
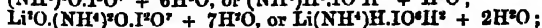
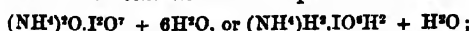
**Dithallic Iodate**,  $(\text{TI}^{\text{I}})^{\text{I}}\text{I}^{\text{O}}\text{O}^{\text{O}}$ , is formed by heating thallious iodate or freshly precipitated thallious oxide with aqueous iodic acid. It is a brownish-grey, heavy, crystalline salt, which is not altered by water, and is nearly insoluble in nitric acid. When heated it gives off water, and behaves in other respects like the thallious salt (Rammelsberg, *Pogg. Ann.* cxlvi. 532).

**Ferric Iodates.** The normal salt,  $\text{Fe}^{\text{O}}\text{O}^{\text{O}}\cdot 3\text{I}^{\text{O}}\text{O}^{\text{O}}$  or  $(\text{Fe}^{\text{O}})^{\text{I}}\text{I}^{\text{O}}\text{O}^{\text{O}}$ , is obtained as a yellow precipitate by heating a solution of ferrous iodide in 5 or 6 pts. water with 2 pts. potassium chlorate dissolved in a little hot water and  $1\frac{1}{2}$  pt. strong nitric acid. It is tasteless, scentless, and perfectly stable. By using smaller quantities of nitric acid, salts are obtained containing smaller proportions of iodic acid; one of a deep red colour appears when dried at  $100^{\circ}$  to contain  $\text{Fe}^{\text{O}}\text{O}^{\text{O}}\cdot \text{I}^{\text{O}}\text{O}^{\text{O}}$ , but decomposes during washing. The salt,  $\text{Fe}^{\text{O}}\text{O}^{\text{O}}\cdot 2\text{I}^{\text{O}}\text{O}^{\text{O}}$  +  $3\text{H}^{\text{O}}$ , obtained by precipitating ammonia-iron alum with potassium or sodium iodate (iii. 302), is somewhat liable to alteration on exposure to the air. These basic salts are converted into the normal salt by digestion with warm dilute nitric acid (C. A. Boll, *Pharm. J. Trans.* [3], i. 624).

**PERIODATES.** K. Ihre (*Deut. Chem. Ges. Ber.* iii. 316) describes the preparation of a number of these salts, all of which have, however, been previously described, except the following:



or  $\text{K}^{\text{O}}\cdot \text{IO}^{\text{O}}\text{H}^{\text{O}} + 3\text{H}^{\text{O}}$ ,  
formed by the action of concentrated alcoholic potash on the salt  $\text{K}^{\text{O}}\text{O}^{\text{O}}\cdot \text{I}^{\text{O}}\text{O}^{\text{O}}$ ;



prepared by the action of barium nitrate and aluminium on the ordinary sodium salt,  $\text{Na}^{\text{O}}\text{O}^{\text{O}}\cdot \text{I}^{\text{O}}\text{O}^{\text{O}}$  +  $6\text{H}^{\text{O}}$ .

With regard to the **triargentic salt**,  $\text{Ag}^{\text{O}}\text{IO}^{\text{O}}$ , described by Fernlund (*1st Suppl.* 746), as produced by boiling the straw-yellow diargentic salt  $\text{Ag}^{\text{O}}\text{H}^{\text{O}}\cdot \text{IO}^{\text{O}}\text{H}^{\text{O}}$  with water, Ihre finds, in accordance with Rammelsberg (*Jahresh.* 1867, p. 166), that the product obtained by boiling the yellow salt with water as long as anything is dissolved is the **pentargentic salt**,  $5\text{Ag}^{\text{O}}\text{O}^{\text{O}}\cdot \text{I}^{\text{O}}\text{O}^{\text{O}}$  or  $\text{Ag}^{\text{O}}\cdot \text{IO}^{\text{O}}\text{Ag}^{\text{O}}$ . From the results of his own experiments and those of other chemists, Ihre concludes that periodic acid forms salts containing either 1, 2, 3, 4 or 5 atoms of metal.

Blomstrand (*Deut. Chem. Ges. Ber.* iii. 317) agrees with this view, which is also in accordance with Thomsen's results (p. 681).

**Thallium Periodates.**—The **thallous salt** has not been isolated. The precipitate

formed either by adding thallous hydrate to periodic acid, or by mixing solutions of thallous nitrate and tetrapotassic periodate, seems to be a mixture of the iodate  $\text{Ti}^{\text{I}}\text{O}_4$ , and the compound  $\text{Ti}^{\text{I}}\text{O}_4^{\text{II}}$ . A thallous salt, said to have the composition  $\text{Ti}^{\text{I}}\text{O}_4^{\text{II}} + 90\text{H}_2\text{O}$ , is formed, as a light-brown precipitate by warming freshly precipitated thallous oxide with periodic acid (Rammelsberg, *vogg. Ann.* cxlvi. 592).

**Periodates of Yttrium and Erbium.**—Two yttrium periodates are formed according as the periodic acid used in their preparation is in excess or not. The most stable, formed with excess of acid, is said to contain  $\text{Y}^{\text{I}}\text{O}_4^{\text{III}} + 24\text{H}_2\text{O}$ ; the other,  $\text{Y}^{\text{I}}\text{O}_4^{\text{II}} + 6\text{H}_2\text{O}$ . Erbium-periodate is said to have the composition  $\text{Eb}^{\text{I}}\text{O}_4^{\text{III}} + 2\text{H}_2\text{O}$  (Clève, *Bull. Soc. Chim.* [2], xix. 193).

**IODOFORM,  $\text{CHI}_3$ .**—This compound treated with bromine at ordinary temperatures gives rise to bromiodoform,  $\text{CIBr}_2\text{I}$ ; but an excess of bromine at high temperatures removes the hydrogen and the whole of the iodine, producing carbon tetrabromide  $\text{CBr}_4$  (Bolas a. Groves, p. 256).

**Iodosulphuric Acid,  $\text{H}^2\text{SO}^3\text{I}^2$ .** (Silvestro Zinno, *N. Repert. Pharm.* xx. 449).—Pelouze a. Frémy obtained the anhydride of this acid,  $\text{SO}^3\text{I}^2$ , by distilling an intimate mixture of iodine and lead sulphite and rectifying the distillate over mercury: the anhydride dissolved in water yielded iodosulphuric acid. Zinno obtains the same acid by dissolving the proper quantity of iodine in concentrated aqueous sulphurous acid; also, by treating iodide of starch with sulphurous acid, and distilling the decolorised liquid. The acid when concentrated at a moderate heat, dissolves sulphur, and acquires thereby a yellow colour.

The iodosulphates of the alkali-metals may be prepared by neutralisation of the aqueous acid with the corresponding bases; the sodium salt also, by adding to a solution of sodium sulphite as much iodine as it is capable of dissolving, keeping the liquid cool; \* also by the action of sodium sulphite on iodide of starch suspended in water.

**Sodium Iodosulphate,  $\text{Na}^2\text{SO}^3\text{I}^2 + 10\text{H}_2\text{O}$ ,** crystallises in colourless elongated perfectly uniform prisms, the taste of which is rather bitter, but much less disagreeable than that of sodium sulphate. 100 parts of water at  $15^\circ$  dissolve 27.5 parts of the salt; it is also slightly soluble in aqueous alcohol. When heated it gives off vapours of iodine, leaving sulphide and sulphate of sodium. With mercuric nitrate it forms a yellowish-white, with silver nitrate a yellow, and with lead acetate a white precipitate (Zinno).

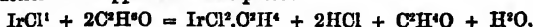
**IRIDIUM. Separation from Platinum.**—The separation of these metals may be effected by the method originally suggested by Birnbaum, which consists in converting them into cyanides, combining the latter with barium cyanide, and then mechanically separating the one double cyanide from the other.

To prepare the cyanides, a mixture of crude iridium oxide and potassium cyanide is fused in a small crucible, and kept at a high temperature until all the metallic oxide is taken up. The fused mass when cold is dissolved in water, filtered from unattacked iridium oxide, and hydrochloric acid is added in sufficient quantity to destroy the excess of potassium cyanide. The liquid is then mixed with concentrated solution of copper sulphate; the violet-coloured precipitate, consisting of the mixed double cyanides of iridium and platinum with copper, is washed by decantation with boiling water; and while it is suspended therein, a strong solution of caustic baryta is added. The copper is thus precipitated as oxide, and the double cyanides of iridium and platinum with barium are formed. Carbonic anhydride is then passed through to precipitate the barium, and the solution concentrated to crystallisation. The yellow platinum salt crystallises first, in small dichroic crystals, and afterwards the iridium salt in large colourless prisms, the crystallisation of both salts being so distinct and separate, that they can easily be picked out one from the other (S. P. Sadtler, *Sill. Am. J.* [3], ii. 338).

**Ethylene-compounds of Iridium.**—Sadtler has endeavoured to prepare iridium-salts analogous to the ethylene-platinum compounds obtained by Zeise (ii. 598). Pure iridium was prepared by igniting the crystals of barium-iridium cyanide obtained as above, and washing out the barium cyanide with boiling water. The metallic iridium,

\* In a note to the abstract of Zinno's paper in the *Jahresbericht für Chemie*, 1871, p. 316, Michaelis says: 'I have had this statement tested by G. Köthe, and it has not been found correct. On adding to aqueous sulphurous acid, either concentrated or dilute, the quantity of iodine required to form iodosulphuric acid, with or without cooling, potassium iodide and sodium sulphate were always formed, and consequently the precipitate formed on adding lead acetate to the liquid was always yellow, not white as stated by Zinno. When on the other hand, a smaller quantity of iodine was added to the solution of sodium sulphite, lead acetate formed a white precipitate. This result, however, was due to the fact that lead iodide and sodium sulphite react so as to form sodium iodide and lead sulphite.'

after having been strongly ignited to effect its oxidation, was heated with nitromuriatic acid to  $200^{\circ}$  in a sealed tube, to convert it into chloride; and this compound was treated with absolute alcohol, with addition of potassium or ammonium chloride. The following reaction then appears to take place:



and the compound  $\text{IrCl}^2.\text{C}^2\text{H}^4$  unites with the chloride of potassium or ammonium. At the same time, however, part of the iridium tetrachloride unites with the ethylene and the alkaline chloride without undergoing reduction to dichloride, so that a mixture of salts is obtained. With ammonium chloride two salts were obtained, agreeing nearly in composition with the formulæ:



With potassium chloride only the salt  $\text{IrCl}^1(\text{C}^2\text{H}^4)^2(\text{KCl})^2$  was obtained, anhydrous, and combined with  $3\text{H}^2\text{O}$ .

**IRON.** *Properties of Pure Iron.*—Caron (*Compt. rend.* lxx. 1263) fused 50 to 150 grams of reduced iron by the heat of a hydrogen gas blow-pipe. The reguli obtained were free from blisters, a proof that hydrogen gas is not absorbed by melted iron. The pure fused iron had a high specific gravity.

	Sp. gr. at $16^{\circ}$
Pure iron (88.879 grams) fused in hydrogen . . . . .	7.880
The same forged . . . . .	7.868
The same drawn out into wire . . . . .	7.847
Pure iron (117.54 grams) fused in a crucible, and therefore exposed to the action of atmospheric oxygen penetrating through the sides of the crucible . . . . .	7.833

Pure iron fused in hydrogen is soft, easily drawn out into wire when cold, very malleable at a red heat. Iron fused in a crucible, on the other hand, is hard, and yields water by prolonged heating in hydrogen, showing that it has absorbed oxygen during fusion in the crucible.

*Action of Cold on Iron.*—Experiments on the action of cold on iron and steel have been made by Brockbank (*Chem. News*, xxiii. 62), Fairbairn (*ibid.* 89), Joule (*ibid.* 101, 143), and Spence (*ibid.* 124). Brockbank concludes that cast iron when cooled below the freezing point exhibits a considerable and increasing loss of tenacity and elasticity. An iron bar which had been exposed to hard frost was incapable of bearing more than one blow of a 12-lb. hammer, whereas when warmed to the temperature of the workshop, it bore fourteen blows of the same hammer without the least sign of fracture. Cold bars appeared crystalline without any indication of fibrous structure, whereas warm bars were fibrous and appeared somewhat crystalline only on the fractured surface. Fairbairn and Joule contradict those assertions, and Spence even comes to the conclusion, that the tenacity of iron is increased by lowering of temperature. The editor of *Engineering*, in which Journal (Feb. 1871, p. 82) the remarks above cited are collected together, observes with reference to them, that on comparing the results of former investigations, and the experience of the railways in Canada, the United States, Russia, and other countries where the winters are severe, there can be but little doubt that cold does diminish the power of iron to resist percussion and shaking, and that this is especially the case with the kinds of iron generally used for wheel-tires, and above all with iron which contains a somewhat considerable proportion of phosphorus. Steel, on the other hand, appears to be less influenced in this way.

#### Compounds of Iron.

**Antimonate.** An amorphous argillaceous mass from Nador, in the province of Constantine in Algeria, contains according to two analyses by Flajolot:—

$\text{Sb}^2\text{O}^3$	$\text{Fe}^2\text{O}^3$	$\text{As}^2\text{O}^3$	$\text{Al}^2\text{O}^3$	$\text{PbO}$	$\text{CaO}$	Loss by ignition
63.50	31.40	—	—	—	—	6.10 = 100
59.30	33.40	2.50	1.80	0.45	trace	3.05 = 100

Flajolot represents these numbers by the formula  $2(\text{Fe}^2\text{O}^3.\text{Sb}^2\text{O}^3) + 3\text{H}^2\text{O}$  (*Compt. rend.* lxxi. 237; *Ann. Min.* [6], xx. 29).

**Ferric Chloride.** From the changes in the depth of colour of solutions of ferric chloride resulting from dilution with water, hydrochloric acid, sal-ammoniac, and a mixture of sal-ammoniac and hydrochloric acid,—also from rise of temperature, and from the age of the solution, A. Müller (*Deut. Chem. Ges. Ber.* ii. 178) infers that ferric chloride in its solutions must undergo chemical alteration. Acetic acid in its action on such a solution exhibits only  $\frac{1}{16}$ th of the energy of hydrochloric acid. Experi-

ments made under similar conditions have shown that 5 mol. acetic acid are capable of displacing 1 mol. sulphuric acid from its combination with ferric oxide: hence it appears that at medium temperature, and in solutions in which it has only a small tension, hydrochloric acid is nearly twice as strong an acid as sulphuric acid. A similar conclusion may be drawn, according to Müller, from the more powerful action of (dilute) hydrochloric acid on cellulose, starch, and sugar.

From former experiments (*J. pr. Chem.* cvi. 321) Müller considers that neutral ferric acetate,  $\text{Fe}^{\circ}\text{O}^{\circ}\cdot 3\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ}$ , can exist permanently in aqueous solution only in presence of a considerable quantity of free acetic acid, and the quantity of the latter must be greater in proportion as there are more salts present which are capable of fixing the acid by formation of acid salts, *e.g.* acetates and sulphates of alkali-metal. Contrary to the ordinary assumption (made in accordance with Berthollet's law), ferric acetate in a solution containing a large excess of acetic acid does not exchange its acid (or only to a slight extent) with the sulphates of potassium, sodium, ammonium, and magnesium, or with the chlorides of sodium, ammonium, barium, and calcium, or nitrate of ammonium. On the contrary, ferric oxide dissolved in acetic acid withdraws phosphoric acid, which at ordinary temperatures is a weaker acid, in greater or lesser proportion from stronger bases (in spite of their excess), and unites with it, in the form of a basic compound, which is gradually precipitated from the acid solution. Any disturbance of the equilibrium of affinity taking place in a solution is slower in coming to an end, in proportion as the affinities of the reacting substances are less energetic.

*Decomposition of Ferric Chloride by Heat in Aqueous Solution* (Krecks, *J. pr. Chem.* [2], iii. 286).

All solutions of ferric chloride are decomposed on heating, the more readily the more dilute they are, the phenomena varying according to the strength of the solutions, the degree of heat to which they are raised, and the length of time during which they are exposed to this heat. The first effect observed in all solutions, when their temperature is raised, is a greater or lesser degree of darkening, owing to the formation of soluble ferric oxide (Graham's oxide) and free hydrochloric acid. If the temperature be now raised still higher, or continued for some length of time at the same degree, the solution becomes turbid, and deposits, according to concentration or temperature, either difficultly soluble ferric oxide (Péan's), or oxychloride, or dense anhydrous ferric oxide. The following table gives the temperatures at which these various phenomena are observed in solutions of different degrees of concentration:—

Concentration in per cent.	Formation of Graham's Ferric oxide	Separation of Péan's Ferric oxide	Formation of oxychloride	Formation of dense Ferric oxide
32	100—130°	—	Above 100°	140°
16	100—120°	—	—	120°
8	100—110°	—	—	110°
4	90—100°	—	90°	?
2	87°	—	87°	?
1	83°	100°—130°	—	—
$\frac{1}{2}$	75°	100°—130°	—	—
$\frac{1}{4}$	64°	—	—	—
$\frac{1}{8}$	54°	—	—	—
$\frac{1}{16}$	36°	—	—	—

Solutions containing  $\frac{1}{16}$  per cent. or less of ferric chloride are decomposed under the influence of light, even at a temperature of 5° or 6° only, though in the dark they keep perfectly at that temperature. Solutions of  $\frac{1}{4}$  per cent. and upwards are permanent when exposed to light at ordinary temperature, and a more or less elevated temperature is required for their decomposition.

The alterations in the specific gravity of solutions resulting from decomposition are in most cases so slight, and the changes taking place so complicated, that but little help can be derived from this property in estimating the amount of change produced. Nevertheless alterations in the specific gravity, due to decomposition, may be observed in solutions of ferric chloride, as shown in the following table, which gives the specific gravities at various temperatures, of two solutions of ferric chloride, each containing  $\frac{1}{4}$  per cent. of the salt. One of the solutions was freshly prepared, the other was old and decomposed:—

*Specific Gravity of Solutions of Ferric Chloride.*

Temperature	Freshly prepared and normal	Old and decomposed	Temperature	Freshly made and normal	Old and decomposed
0	1.00086	1.00060	60	—	0.98468
10	1.00080	1.00041	70	—	0.97937
20	0.99888	0.99850	80	—	0.97394
30	0.99682	0.99644	90	—	0.96776
40	0.99452	0.99386	100	—	0.96114
50	—	0.98920	—	—	—

The property possessed by colloid ferric oxide, to be precipitated from its solutions by the addition of neutral salts of the alkalis, discovered by Graham, affords, however, the means of estimating the amount of colloid oxide present in a solution; and after its removal the amount of unaltered ferric chloride remaining may be estimated as usual. Since solutions containing more than 1 per cent. require to be heated to a temperature above  $100^{\circ}$  before they are decomposed, the experiments were limited to solutions containing 1 and a  $\frac{1}{2}$  per cent. of ferric chloride respectively. The solutions were heated in an apparatus which permitted a careful regulation of the temperature, and allowed the taking of samples at any desired temperature, at the same time preventing any evaporation. The experimental results may be summed up as follows:—

1. In solutions of ferric chloride the amount of decomposition produced increases with the rise in temperature, but is not proportional to this rise.

2. With a constant temperature the amount of decomposition increases with the time up to a certain maximum. The increase is rapid at first, becomes gradually slower, and reaches the maximum after the lapse of about twelve hours.

The method sometimes employed for separating ferric oxide from manganese, cerium, nickel, and cobalt, by carefully neutralising the solution with ammonium or sodium carbonate, and boiling, whereby the ferric oxide is precipitated, while the other metals remain in solution, may be regarded as depending on the formation of colloid ferric oxide, which is then precipitated by the alkali-salt present. The method proposed by Hofmann and Frankland of purifying sewage by the addition of ferric chloride also illustrates the same phenomena. The very dilute solution of ferric chloride produced is decomposed, as before described, even at ordinary temperature, and the ferric oxide precipitated carries down the other impurities.

On the decomposition of ferric salts by heat, see also Tichborne (*Chem. News*, xxix. 209).

**Nitrosulphides.** Roussin, by dropping a solution of a ferric salt into a mixture of ammonium sulphide and potassium nitrite, obtained a salt (dinitrosulphide of iron) in black needle-shaped crystals to which he assigned the formula  $\text{Fe}^3\text{S}(\text{N}^2\text{O})_2 \cdot \text{H}^2\text{S}$  or  $\text{FeSN}^2\text{O}^2 \cdot \text{Fe}^3\text{S}^2\text{N}^2\text{O}^2 \cdot \text{H}^2\text{S}$  (iii. 301). According to Porczynsky (*Ann. Ch. Pharm.* cxv. 302; *Jahresb.* 1863, 259) this salt has the composition  $\text{Fe}^3\text{S}^2(\text{N}^2\text{O})_2 \cdot 2\text{H}^2\text{O}$  or  $\text{Fe}^3\text{S}^2\text{Fe}^3\text{S}^2(\text{N}^2\text{O})_2 \cdot 2\text{H}^2\text{O}$ , and when treated with potash gives off ammonia, and yields black triclinic crystals of the potassium salt,  $\text{K}^1\text{S} \cdot \text{Fe}^3\text{S}^2(\text{N}^2\text{O})_2$ . Rosenberg (*Deut. Chem. Ges. Ber.* iii. 312) assigns to Roussin's salt the more complex formula  $\text{Fe}^3\text{S}^2(\text{N}^2\text{O})_2 \cdot \text{H}^2\text{O}$ , and to the potassium salt obtained by treating it with potash, the formula  $\text{K}^1\text{Fe}^3\text{S}^2(\text{N}^2\text{O})_2 + 19\text{H}^2\text{O}$ . The corresponding sodium salt has the formula  $\text{Na}^1\text{Fe}^3\text{S}^2(\text{N}^2\text{O})_2 + 24\text{H}^2\text{O}$ .

**Oxides. Monoxide or Ferrous oxide.**—This oxide may be obtained in the anhydrous state by the action of carbon dioxide on pure iron at a red heat:



The oxide thus obtained is black, crystalline, and magnetic, and agrees exactly in composition with the formula  $\text{FeO}$ . Heated to redness in the air, it is converted into  $\text{Fe}^2\text{O}^3$  (Tissandier, *Compt. rend.* lxxiv. 531).

**Ferric Oxide.**—A native compound of this oxide with cuprous oxide, named *Deafossite*, is contained in the mineralogical collection of the *École des Mines*, and in that of the *Musée d'Histoire Naturelle* at Paris. It consists of 47.99 p.c.  $\text{Fe}^2\text{O}^3$ , 3.52  $\text{Al}^2\text{O}^3$ , and 47.45  $\text{Cu}^2\text{O}$ , agreeing with the formula  $(\text{Fe}; \text{Al})^2\text{O}^3 \cdot \text{Cu}^2\text{O}$ . Sp. gr. = 5.07; hardness = 2.6; streak, greyish-black. It splits easily into very thin perfectly opaque laminae, soils the fingers, dissolves easily in acids.

Attempts to prepare this mineral artificially by heating a solution of ferric chloride with cuprous oxide to  $250^{\circ}$  in a sealed tube resulted in the formation of *atacamite*, the iron being all precipitated. This may possibly be the natural mode of formation

of atacamite,  $\text{Cu}^2\text{ClH}^2\text{O}^2$ , especially as it is often found associated with ferric oxide (Friedel, *Compt. rend.* lxxvii. 211).

**Ferroso-ferric Oxides.**—H. Sainte-Claire Deville (*Ann. Ch. Pharm.* clvii. 71) has examined the action of water on iron and of hydrogen on ferroso-ferric oxide. The apparatus employed for oxidation-experiments consisted of a glass or porcelain tube containing the iron, and communicating at one end with a Geissler's or Sprengel's air-pump, at the other with a retort containing water kept at a constant temperature by surrounding the retort with ice or cold water. For reduction experiments the iron was replaced by ferroso-ferric oxide and the retort by a hydrogen-apparatus. The tube containing the iron or oxide was kept at a constant temperature by immersion in an oil- or mercury-bath for the lower temperatures, and for higher temperatures by means of the vapour of mercury ( $360^\circ$ ), sulphur ( $440^\circ$ ), cadmium ( $860^\circ$ ), zinc ( $1040^\circ$ ); for the highest temperature the tube was exposed to the direct flame of petroleum, the flow of which was regulated by stop-cocks. As soon as the tension of the gases became constant at any particular temperature, it was measured, and thence the tension of the dry hydrogen could be calculated, since the tension of the aqueous vapour was known from the temperature of the water in the retort, which was always lower than that of the other parts of the apparatus.

The following table gives the results of Deville's experiments, placed together in pairs: the numbers in the first line of each pair relating to a water-temperature of  $0^\circ$ , that in the second to a somewhat higher temperature, between  $10.6^\circ$  and  $19^\circ$ . This table shows (1) the temperature of the iron for each pair of experiments; (2) the tension of the water-vapour  $e$  and  $e'$ , as well as the tension of the dry hydrogen  $h$  and  $h'$ ; (3) the relation  $r = \frac{h}{e}$  and  $r' = \frac{h'}{e'}$ , that is, the ratio of the tension of the hydrogen to that

of the water-vapour, and lastly (4), the ratio  $\frac{r'}{r}$ , which is an expression of the alteration taking place in the relative quantities of the hydrogen- and water-vapours when the tension of the latter is altered while the temperature of the iron remains constant.

Temperature of the Iron	Tension of the Water-vapour $e$	Tension of the dry Hydrogen $h$	Ratio of the Tensions $r = \frac{h}{e}$	Ratio $\frac{r'}{r} = \frac{e}{e'}$
200°	{ 4.6	195.9	20.848	0.965
	{ 9.7	95.3	20.134	
265°	{ 4.6	64.2	13.966	1.073
	{ 15.7	235.1	14.974	
360°	{ 4.6	40.4	8.783	0.915
	{ 9.5	76.3	8.031	
440°	{ 4.6	25.8	5.609	1.022
	{ 10.1	57.9	5.732	
860°	{ 4.6	12.8	2.783	0.661
	{ 13.1	23.9	1.838	
860°	{ 4.6	12.8	2.783	0.656
	{ 12.7	23.2	1.827	
1040°*	{ 4.6	9.2	2.000	0.752
	{ 12.7	10.1	1.804	
1040°	{ 4.6	9.4	2.043	0.667
	{ 12.7	17.3	1.362	
1600°	{ 4.6	5.1	1.109	0.647
	{ 13.3	11.7	0.718	

The numbers in this table show that iron decomposes less water the higher it is heated, and that when the tension of the water-vapour is increased (by heating the water in the retort) the tension of the hydrogen likewise increases, and that the higher the temperature of the iron, the less is the increase in the tension of the hydrogen compared with that of the aqueous vapour.

The total result is independent of the quantity of iron or iron oxide employed, and the tensions of the hydrogen gas and aqueous vapour are always in the same ratio to one another so long as the temperature remains constant. This state of equilibrium is the same at a given temperature whether aqueous vapour be made to act upon iron or hydrogen upon iron oxide.

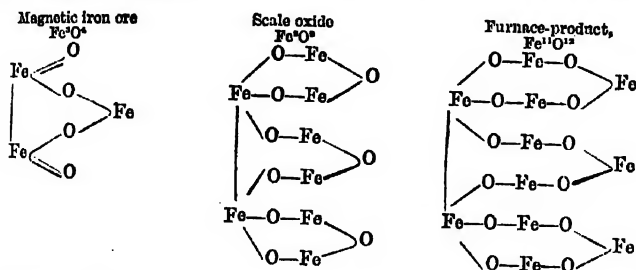
\* In these two experiments iron oxide was reduced by hydrogen; in all the others, water acted on metallic iron.



**Furnace-product containing Magnetic Oxide of Iron.**—This mineral was found in a cleft of the hearth-stone (consisting of quartz and clay) of the coke-fed blast-furnace of Prevali in Carinthia, and had doubtless been formed there. It consists of fine steel-grey closely intergrown crystals, strongly magnetic and having a sp. gr. of 5.63. It gave by analysis 76.2 p.c. Fe and 23.8 O, or 79.83 FeO and 20.11  $\text{Fe}^{\text{II}}\text{O}^{\text{II}}$  (H. Völker, *Ann. Ch. Pharm.* clxv. 356).

Lieben, in a note to Völker's paper, observes that the occurrence of crystallised magnetic iron oxide as a furnace-product has often been noticed before, but that such products have hitherto been found to agree in composition with the natural mineral  $\text{Fe}^{\text{II}}\text{O}^{\text{II}}$ , or  $\text{FeO}.\text{Fe}^{\text{II}}\text{O}^{\text{II}}$ . The product above described differs, however, both from this and from the common scale-oxide (generally regarded as  $\text{Fe}^{\text{II}}\text{O}^{\text{II}}$  =  $6\text{FeO}.\text{Fe}^{\text{II}}\text{O}^{\text{II}}$ , or by some chemists as  $\text{Fe}^{\text{II}}\text{O}^{\text{II}}$  =  $4\text{FeO}.\text{Fe}^{\text{II}}\text{O}^{\text{II}}$ ), its specific gravity being higher, and its composition agreeing with the formula  $\text{Fe}^{\text{II}}\text{O}^{\text{II}}$  or  $9\text{FeO}.\text{Fe}^{\text{II}}\text{O}^{\text{II}}$ .

The constitution of these three varieties of ferroso-ferric oxide may be represented by the following formulæ:—



**Absorption of Salts from Solution by Ferroso-ferric Oxide.**—Official ferroso-ferric oxide completely absorbs the nitrates of lead, silver, copper, and zinc, also zinc chloride and the sulphates of copper, ferrosus, and zinc. Common alum, chrome-alum, and tartar-emetac, are decomposed by the oxide in such a manner that the filtrate contains sulphate or tartrate of potassium. The salts above mentioned cannot be washed out of the iron oxide by water either cold or hot. The salts of the alkaline earth-metals are slowly absorbed, those of magnesium and the alkali-metals, also mercuric chloride, not at all. Ignited ferroso-ferric oxide appears to exert this absorbing power less strongly. Ferroso-ferric oxide likewise absorbs organic matters with great facility (J. B. Schöber, *N. Rep. Pharm.* xix. 345).

**Estimation of Iron and Analysis of its Compounds.** 1. *Estimation by means of Soluble Ferrocyanides.*—When to a solution of potassium ferrocyanide, with or without the addition of a mineral acid, a ferric solution is slowly added, the blue precipitate at first formed disappears again, the solution remaining blue and clear; on further addition it becomes muddy, but still always preserving its character as a blue solution, till suddenly a drop more of the iron solution causes sudden coagulation, the liquid soon separating into a clear colourless layer, and the blue flocculent precipitate settling to the bottom. In the clear solution neither iron nor ferro-cyanogen is present. This coagulation may, therefore, be used as an indication of the termination of the reaction. The experiment is best made in a porcelain basin.

To determine the quantitative relation of this reaction and its applicability to the estimation of iron and of ferro-cyanogen, solutions of known strength were prepared from pure potassium ferrocyanide and ammonio-ferrous sulphate. The latter was oxidised with nitric acid. Of the two salts 0.1 gram-equivalent was taken, i.e. 2.11 grams of the former and 1.96 gram of the latter dissolved to 530 c.c. Experiment showed that 26 c.c. of the potassium ferrocyanide solution required for complete decomposition 32.3 c.c. of the iron solution, consequently that the number of equivalents of ferro-cyanogen and iron concerned in the reaction are as 26 : 32.3, or nearly as 3 : 4; in other words, that 3 eq. ferro-cyanogen require 4 eq. Fe or 2 eq.  $\text{Fe}^{\text{II}}\text{O}^{\text{II}}$ . To obtain concordant results, the solution of the ferro-cyanide must be diluted with water to a certain extent, or the reaction denoting the completion of the experiment will be obtained too soon, i.e. the quantity of ferric solution required to attain this point will be less than that which is equivalent to the ferro-cyanogen present. The addition of acid is requisite even when the above precaution is observed. (H. Rheineck, *Dingl. pol. J.* cii. 164).

2. *Estimation of Ferrous Oxide in presence of Ferric Oxide in Silicates.*—For this purpose Wilbur a. Whittlesey (*Chem. News*, xlii. 2) mix  
2nd Sup.

the finely pounded silicate in a platinum crucible with an equal or a larger quantity of pulverised fluorspar or crysolite, and such a quantity of hydrochloric acid that the crucible is about two-thirds filled by the mixture. The crucible is placed on a water-bath and heated in a stream of carbon dioxide or coal-gas till all the iron is dissolved, which takes place in  $\frac{1}{2}$  to  $1\frac{1}{2}$  hour, according to the nature of the mineral. The ferrous oxide is then estimated by titration in the ordinary way with solution of permanganate. The method of solution here described is said to be applicable even to ferric oxide which has previously been ignited.

H. Allen (*ibid.* 57) regards this method as very exact, but suggests that it is better to titrate the solution of ferrous chloride with potassium bichromate, since, as is well known, the titration with permanganate does not always give exact results, excepting when the iron oxide is dissolved in sulphuric acid. Difficultly soluble ferrous compounds may be dissolved by heating them with hydrochloric acid under pressure. The finely powdered substance is sealed up in a glass tube with fuming hydrochloric acid and heated, first in a water-bath, then to  $140^{\circ}$ – $150^{\circ}$ .

3. *Analysis of Chrome-Iron Ore.*—To estimate the iron and chromium in this ore, J. Blodget-Britton (*Chem. News*, xxi. 266) mixes 0.5 gram of the finely pounded substance with 4 grams of a flux consisting of 1 part potassium chlorate and 3 parts soda-lime, and heats the mixture to bright redness in a platinum crucible for an hour and a half or longer. The mass, which does not fuse and is easily loosened from the crucible by gentle tapping, is to be finely pulverised and drenched in a beaker glass with 18 c.c. of water, the whole boiled for two or three minutes, and mixed, on cooling, with 15 c.c. of hydrochloric acid of ordinary strength, which, on stirring, dissolves the whole, except a little gelatinous silica.

a. To estimate the chromium, the liquid containing all the iron and chromium in the highest state of oxidation is diluted to 3 ounces in a porcelain basin, and a solution of 1 gram of metallic iron in dilute hydrochloric acid is added, mixed with a quantity of water sufficient to raise the volume of the entire liquid to 8 ounces. On titrating with permanganate, the difference between the quantity of iron found and that which was weighed out gives the quantity of iron converted into ferric oxide by the chromic acid. Every 1 part of ferric oxide thus formed represents 0.320 part metallic chromium, or 0.4663 chromic oxide. The iron, in the form of turnings, is dissolved in a test-tube closed with a caoutchouc stopper, through which there passes a glass tube bent at right angles. To accelerate the reaction, and at the same time exclude the air, the liquid is heated to boiling.

$\beta$ . To estimate the iron, the mineral, ignited with the flux as before, is dissolved in 15 c.c. hydrochloric acid after boiling with 10 c.c. water; the whole of the iron and chromium are reduced by zinc after cooling; and the resulting ferrous salt is titrated with permanganate. For diluting the liquid previous to this last operation, cold water acidulated with sulphuric acid is used, as the end of the reaction is thereby rendered more distinct.

4. *Analysis of Pig-Iron and Steel.* a. *Estimation of the Iron.*—F. Kessler (*Zeitschr. anal. Chem.* xi. 249–270) effects this by a modification of the volumetric method depending on the use of potassium bichromate. Pure potassium bichromate is prepared by fusing the salt in a glass bulb placed in a bath of fused bichromate; the inner part of the salt thus prepared is found to be perfectly dry and undecomposed. A weighed quantity of this pure salt is added to the solution containing the iron (reduced to the ferrous state by the action of stannous chloride, excess of this latter being decomposed by the addition of mercuric chloride), and then a normal solution (4.01 gram per litre) of the bichromate is run in. The end of the reaction is noted by adding excess of bichromate, then a ferrous chloride solution till the blue colour with potassium ferricyanide reappears. If copper be present in any quantity, it must be removed by precipitation with sulphuretted hydrogen, before the iron is estimated. Kessler estimates the oxidation-equivalent of potassium bichromate as equal to 49.1.

$\beta$ . *Estimation of Manganese.*—For this purpose Kessler employs the following solutions:—

a. A decinormal solution of potassium permanganate, containing 3.16 grams of pure salt per litre.

$\beta$ . A solution of antimonious chloride, prepared by dissolving 14.6 grams of pure antimonious oxide in concentrated hydrochloric acid, and diluting to 1 litre. This solution is titrated against the permanganate.

Solutions of sodium carbonate, sulphate, and acetate are required, containing respectively 200 and 600 grams of the crystallised salts per litre; also concentrated and dilute acetic and hydrochloric acids, sulphurous acid, and saturated bromine water. 0.66 gram of the iron or steel is dissolved, the solution diluted to 100 c.c., and neutralised with sodium carbonate solution, until a slight permanent precipitate is pro-

duced; this is dissolved by cautious addition of dilute hydrochloric acid; 1.2 c.c. of concentrated sodium acetate solution and 1.2 c.c. acetic acid, or in their place 3 c.c. of sodium sulphate solution are then added, and the liquid, after dilution and boiling, is made up to 300 c.c. and filtered. 250 c.c. (= .55 gram of the substance) are placed in a 600 c.c. flask; 150 c.c. water, 100 c.c. bromine-water, and 2 c.c. sodium acetate solution added; after an hour, 6 c.c. of the latter solution are added, and at the end of another hour, 12 c.c. of the same substance; the liquid is then warmed in the water-bath till all excess of bromine is driven off. The precipitate is collected and well washed with dilute solution of sodium acetate. The filter, with the precipitate, is then treated in a porcelain basin with 5, 10, or 15 c.c. of the antimony solution, 15 c.c. strong hydrochloric acid are added after a while, and the whole is digested till no trace of an undecomposed precipitate remains. 100 c.c. water are then added, and the solution titrated with the permanganate solution. If the process is thus carried out, half the difference between the number of c.c. permanganate corresponding with the c.c. of antimony solution used, and the number of c.c. of permanganate actually employed, gives the percentage of manganese (1 c.c. of the permanganate being equal to 0.5 per cent. manganese).

Cobalt, nickel, or copper, if present, is precipitated together with the manganese; but, except in the case of cobalt, their influence on the manganese estimation is scarcely perceptible.

*Colorimetric Estimation of the Manganese.*—Pichard (*Compt. rend.* lxxv. 1821) describes a method depending essentially on the conversion of the manganese into an alkaline permanganate, and the comparison of the colour of the resulting solution with that of a similar solution containing a known weight of manganese: 0.1 gram of finely divided material is first carefully oxidised by calcination, and then fused with 2 or 3 decigrams of sodium carbonate. The mass is dissolved in 5 c.c. of nitric acid, to which one drop of hydrochloric acid has been added, and the manganese is oxidised after the addition of 10 c.c. of water, by boiling the solution for a short time with 0.5 gram of lead peroxide. The clear liquor is subsequently decanted into a test-glass graduated into 500 c.c. The standard solution of permanganate is prepared of such a strength that 10 milligrams of manganese are contained in 1 litre of the solution.

Specimens of iron, or of iron-ore, seldom contain more than 5 per cent. of manganese. If, therefore, 0.1 gram of material be taken for analysis, and the solution obtained therefrom be diluted until the tint corresponds exactly with that of the standard liquor, then every 100 c.c. observed will represent 1 per cent. of manganese in the sample under examination.

*γ. Estimation of Carbon in Cast Iron and Steel.*—The mode of estimating the carbon by dissolving the iron in cupric chloride and oxidising the separated carbon by a chromic acid solution (iii. 372), has been modified by A. H. Elliott (*Chem. Soc. J.* [2], vii. 182). To avoid the loss of carbon, which may possibly result from the elimination of part of it in the form of hydrocarbons by the action of the free acid in the cupric chloride solution, Elliott uses a solution of cupric sulphate, which does not contain free acid. He then removes the precipitated metallic copper by means of cupric chloride, before proceeding to oxidise the carbon with chromic acid solution.

Eggertz (*Dingl. pol. J.* clxxx, 350) has devised a colorimetric method of estimating the carbon, founded on the fact that cast iron and steel dissolve in nitric acid with a brown colour darker in proportion to the quantity of carbon they contain: 0.1 gram of the iron or steel is dissolved, with aid of heat, in nitric acid of sp. gr. 1.2, and the brown colour of the solution is compared with that of a solution of cast steel containing a known amount of carbon, both being diluted to the same degree.

This method has been modified by J. B. Britton (*Dingl. polyt. J.* cxi. 182) as follows:—He uses sixteen glass tubes, 2½ inches long and ¼ inch diameter, placed in a wooden stand; these tubes are filled with a mixture of alcohol and water coloured with burnt coffee. The solution in the first tube at the left side corresponds in colour with a liquid containing 1 gram of iron with 0.5 per cent. combined carbon dissolved in 15 c.c. nitric acid. The liquid in the next tube to the right corresponds with the same amount of iron, but containing .07 per cent. combined carbon, dissolved in the same amount of nitric acid, and so on, each solution varying in colour so as to correspond with an increase of 0.2 per cent. carbon. The back of the stand is covered with thick white paper.

The sample to be tested must be obtained in fine powder, 1 gram dissolved in 15 c.c. pure nitric acid of specific gravity 1.42, diluted with 30 c.c. water. This solution is filtered into a test-tube 4 inches long and of a diameter the same as that of the tubes in the stand, and the depth of colour is compared with that of the standard solution. Care must be taken that the nitric acid used is always of the strength given above.

that the liquid to be tested is at the ordinary atmospheric temperature, that the testing is performed soon after dissolving the sample, and that all circumstances under which the standard solutions and the solutions of the samples are made, are the same in both cases.

W. D. Hermann (*Chem. Soc. J.* [2], viii. 376) considers that the carbon in steel may be most correctly estimated by combustion in a stream of oxygen, the carbon dioxide thereby produced being absorbed as usual by caustic potash. The iron is at the same time oxidised to ferric oxide, the amount of which is very constant, and serves as a check on the completeness of the combustion.

8. *Estimation of Sulphur and Phosphorus in Iron.*—A. H. Elliott estimates the sulphur by liberating it in the form of hydrogen sulphide, absorbing the gas in a solution of pure soda (prepared from sodium) and determining the hydrogen sulphide in the acidified solution by means of a standard solution of iodine (*Chem. News*, xxiii. 76).

Meineke (*Zeitschr. anal. Chem.* x. 280) dissolves the iron by means of a solution of cupric chloride, and determines the sulphur and phosphorus by precipitation.

5 grams of iron in fine powder are dissolved in from 1 to 1½ hour by gentle warming with a concentrated solution of cupric chloride. After carefully decanting off the iron solution, the separated copper is removed by the renewed addition of cupric chloride, cuprous chloride being formed, which is kept in solution by adding common salt.

The insoluble residue is separated by means of an asbestos filter, washed, thrown with the filter into a beaker, oxidised with strong nitric acid and chlorate of potassium, evaporated to dryness; and in the solution filtered therefrom the sulphur is estimated as barium sulphate. To the filtrate ammonia is added, which precipitates iron oxide together with the phosphoric acid; this precipitate is dissolved in hydrochloric acid, and the phosphoric acid estimated by a molybdic acid solution.

The results obtained by this method show a somewhat higher percentage of sulphur than those obtained by the older process of driving off the sulphur as sulphuretted hydrogen, absorbing it in an ammoniacal silver solution, and estimating the sulphur in the silver sulphide formed. Meineke therefore supposes that, in the old process, there always remains a certain amount of sulphur not driven off as sulphuretted hydrogen.

If phosphorus only is to be estimated, the insoluble residue together with the separated copper is washed, oxidised as formerly, and evaporated to dryness with hydrochloric acid, and the residue is treated with aqueous ammonia. There is always sufficient iron oxide present to precipitate all the phosphoric acid. In the hydrochloric acid solution in which the precipitate is re-dissolved, phosphoric acid is estimated by a molybdic acid solution.

F. Kessler (*Deut. Chem. Ges. Ber.* iii. 11) precipitates the iron and accompanying metals in acid solution with potassium ferrocyanide, and estimates the phosphorus in the filtrate: 5.6 grams of the iron or steel are dissolved in nitric acid; the liquid is evaporated to dryness; the residue dissolved in hydrochloric acid; the ferric solution reduced with hydrogen sulphide; 42 grams of potassium ferrocyanide are added; and the whole is diluted to 518 c.c. (the precipitate occupies 18 c.c., and therefore the solution is diluted to 518 and not merely to 500 c.c.). 250 c.c. of the filtrate mixed with magnesium sulphate and ammonia yield crude ammonio-magnesian phosphate, which must be purified by solution in nitric acid, filtration, and precipitation with ammonia, and converted by ignition into magnesium pyrophosphate: ¼ decigram answers to 1 p.e. phosphorus in the iron. For further details of the process, see *Chem. Soc. J.* [2], x. 80.

e. *Estimation of Silicon.*—H. Boussingault estimates the amount of silicon in cast iron and steel in the dry way. A quantity of the iron weighed out in a platinum boat is oxidised by ignition for several hours in a muffle, and the resulting oxide is moderately heated in a stream of dry hydrogen chloride. The iron is thereby volatilised as chloride, while the silica remains as a pure white mass having the structure of the iron particles. The purity of the silica may be tested by moistening it with hydrofluoric acid and a drop of sulphuric acid, and heating it; if pure, it will volatilise without residue (*Ann. Chim. Phys.* [4], xxii. 457).

**IRON METALLURGY. I. Cast or Pig Iron.** 1. *Chemistry of the Blast-Furnace.*—Several important points relating to the Chemistry of the Blast-Furnace have been explained by I. Lowthian Bell in a Lecture delivered before the Chemical Society, June 1869 (*Chem. Soc. J.* [2], vii. 208). He disputes the correctness of the assumption made by Scheerer, Tunner, and Ebelmen, respecting the existence of different zones of action in the blast-furnace,—namely, an upper zone, in which the reduction of the ore takes place, and a lower one, in which the reduced iron becomes carbonised,—on the ground that such an assumption implies the descent of

all the lumps of ore at a uniform rate. This, however, is prevented by the friction of the lumps against the sides of the furnace, and by their different forms and sizes; it is likewise at variance with all practical experience. Neither is it possible to admit the existence of distinct zones of temperature, inasmuch as the temperature at any particular part must vary with the different chemical processes which go on, now in one part, now in another, accordingly as the stream of hot gases meets with greater or less resistance. Mr. Bell's experiments indicate that the temperature required for the reduction of iron oxide has hitherto been estimated too high. Cleveland iron ore, in lumps of the size of hemp-seed, converted carbon monoxide almost completely into dioxide, even at 300° C. and lost in 15 minutes 39 p.c. of its oxygen. In the gases from the blast-furnace the reduction of various iron ores began at the melting point of bismuth, more quickly at that of zinc; but experiments made with ores in perforated boxes according to the method of Tunner and Ebelmen, gave much less reduction at the same temperatures.

Mr. Bell further denies that hydrogen, ammonia, or cyanogen, plays any essential part in the reduction of the ore. He finds that the temperature at which iron separates carbon from its monoxide is lower than it has been placed by former observers, and that it lies between the melting points of lead and zinc (i.e. at about 360°). The union of the iron with carbon takes place simultaneously with its reduction, and the conversion of the carbon into graphite depends only on the temperature at which the fusion and subsequent cooling take place.

The composition of the gases collected at different depths of a blast-furnace exhibits considerable variation; and it is only from the composition of those which issue from the mouth that any trustworthy inference can be drawn respecting the chemical changes going on in the furnace.

The saving of fuel by the use of the hot blast appears, from Mr. Bell's observations, to be due, not to the production of a comparatively high temperature, but to the fact that the fuel which serves to heat the blast is completely burnt, and gives up all its heat of combustion to the blast; whereas, in the furnace, the final product of the combustion is only the monoxide, not the dioxide of carbon, and consequently the heating effect of the same quantity of carbon is reduced to one-third of its total amount. Moreover, the gases from the mouth of a furnace worked with the hot blast carry away less heat than those from a cold-blast furnace, probably because the specific heat increases rapidly with rise of temperature, and an increased charge of ore involves greater absorption of heat. As a consequence of the preceding considerations, and in accordance with extended experience, it is recommended that the height of blast-furnaces be increased beyond their usual limits.

**2. Utilisation of the Residues from the Burning of Iron Pyrites for Smelting in the Blast-Furnace.**—An account of experiments made for this purpose is given by E. Richters (*Dingl. pol. J.* cxcix. 292; *Jahresb. f. Chem.* 1871, 991). These residues usually contain from 3 to 6 p.c. sulphur, partly in the form of iron monosulphide, or, if the pyrites contained blende, in the form of unaltered zinc sulphide or of basic zinc sulphate. Arsenic and copper are also often present. The copper must be removed before the residues are smelted for iron. The experiments were made in a blast-furnace in which 450 cwts. of iron were smelted daily with a blast-pressure of 4 lbs. per square inch, a blast-temperature of 300°–400° C., a consumption of coke amounting to 150–160 lbs. to 100 lbs. of pig-iron, and with a production of slag amounting to between 100 and 110 lbs. In addition to the sulphur contained in the pyrites residues, a considerable quantity was also introduced into the charge from the ash of the coke, which contained from 10 to 12 p.c. sulphuric acid.

The ore mixed with the pyrites residues consisted of magnetic iron ore, a small quantity of black band, roasted clay ironstone, bog iron ore, and red hematite. The working of the furnace was greatly impeded by the complete want of manganiferous ores, which are well known to assist in carrying the sulphur into the slag. The facility of this transference of the sulphur from the charge to the slag depends very much on its mode of occurrence. Sulphur belonging to the ore passes into the iron much more easily than that which is contained in the fuel or the fluxes. A high temperature of the zone of fusion, and a basic constitution of the charge, are the chief conditions for obtaining iron as free as possible from sulphur from a charge rich in sulphur.

In the experiments under consideration the object in view was to obtain a pig-iron containing not more than 0.04 p.c. sulphur, such as could be used in Bessemer steel works. The experiments were so conducted that the proportion of pyrites residues in the charge, and the proportion of lime were gradually increased, till, on the one hand, further addition of lime was forbidden by the difficult fusibility of the slag, and, on the other, the proportion of sulphur in the iron began to exceed the maximum assigned. A charge which, independently of the coke, contained 38.0 p.c. roasted magnetic iron ore, 25.5 p.c. pyrites residues (with 1.63 p.c. sulphur), 1.5 p.c. raw black-band, and

35.0 p.c. limestone, and in which, including the coke-ash, 4.6 parts of sulphur were present to 100 parts of iron, yielded a grey graphitic pig-iron containing 0.022 p.c. sulphur. But as soon as the temperature of the zone of fusion was lowered, the slags became more basic, and pig-iron was obtained containing a higher proportion of sulphur. The difficulty of transferring the sulphur to the slag does not increase in proportion to the amount of sulphur present. An increase of 0.5 to 1 p.c. in the charge may be removed by increasing the basicity of the charge from 0.1 to 0.2 p.c.

To obtain iron still more free from sulphur, a number of favourable influences must co-operate, especially a high temperature. The same charge yielded at different temperatures pigs containing 0.049, 0.088, 0.096, and 0.224 p.c. sulphur. In the charge above specified the maximum quantity of lime was added, and the slag thereby rendered difficultly fusible. To ascertain whether, with the use of a given quantity of lime, a more acid and more fusible slag might not be used, clay capsules from a porcelain manufactory were added to the charge. It was found, however, that, according to the quantity of burnt clay added, the amount of sulphur in the pig was increased to 0.037 and even to 0.110 and 0.146 p.c.

The pig-iron obtained in these experiments was very rich in silicon: a result due simply to the circumstance that the proportions of the charge which tend to remove sulphur from the iron are exactly those which tend to introduce silicon into it. The smallest proportion of sulphur in the iron obtained was 0.013 p.c., and this iron contained 3.485 p.c. silicon.

Richters has also analysed a blast-furnace slag very rich in sulphur, and the iron obtained from it, with the following results:—

Slag	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	FeO	MnO	CaS
	33.18	13.28	42.63	5.93	0.22	0.04	5.90
Pig-iron	Fe	C (graphite)	Mn	Si	P	S	
	93.631	4.021	0.791	0.961	0.246	0.079	

The slag was crystalline, light grey, and smelt strongly of hydrogen sulphide, especially when pounded. Although very basic, it did not disintegrate in contact with the air. The 5.90 p.c. calcium sulphide contained in it answers to 2.62 p.c. sulphur. Nevertheless, the proportion of sulphur in the iron smelted from it did not exceed the ordinary limits. The result shows that even with a highly sulphuretted raw material a good iron may be obtained by proper adjustment of the basicity of the charge.

3. *Composition of Pig-Iron.*—Investigations on the influence of the elements associated with iron in the pig, and the part they play in the conversion of the pig into wrought iron and steel, have been published by E. Riley (*Chem. Soc. J.* [2], x. 533).

Analyses of different numbers or qualities (No. 1 denoting the best quality) of cold-blast pig-iron from the Low Moor Bowling works in Yorkshire, show that the composition in the different numbers is practically the same, the only apparent difference being a slight decrease in the proportion of silicon as the quality becomes lower.

#### Bowling Pig-Iron.

	1	2	3	4
Carbon, as graphite	3.421	3.155	3.361	3.308
Carbon, combined	0.583	0.581	0.393	0.319
Silicon	1.708	1.646	1.382	1.381
Iron	92.070	92.644	92.962	93.292
Manganese	1.606	1.472	1.475	1.169
Phosphorus	0.630	0.636	0.602	0.602
Sulphur	0.073	0.073	0.070	0.081
Titanium	trace	trace	trace	trace

The diminution in percentage of silicon with the quality of the iron is much more apparent in hot-blast pig, as may be seen from the following analyses of Seend pig, which likewise show that the proportion of sulphur is greater in the lower qualities:—

#### Pig-Iron from Seend, Wiltshire.

	Silicon	Sulphur	Phosphorus
1	4.717	0.86	0.87
2	3.659	0.77	0.17
3	3.209	0.96	0.68
4	3.140	1.06	0.72
5	2.257	1.60	0.26
6	2.197	2.48	0.89

In Welsh pig-iron also the percentage of sulphur increases as the quality of the pig deteriorates.

*Analyses of South Wales Pig from Clay Ironstone.*

	Gray	Mottled	White	Gray
Carbon . . . . .	3.14	2.95	2.84	3.08
Silicon . . . . .	2.16	1.96	1.21	2.22
Sulphur . . . . .	0.11	0.28	0.46	0.09
Phosphorus . . . . .	0.63	0.63	0.64	0.63
Iron . . . . .	94.56	95.39	95.10	94.35
Manganese . . . . .	0.50	0.23	0.14	0.33
Nickel and Cobalt . . . . .	0.05	0.04	0.03	0.07
	101.15	101.48	100.42	100.77

These results tend to show that the difference between grey and white cast iron is due, at least in part, to the larger proportion of sulphur in the latter. Difference of temperature in the smelting has, however, some effect, a high temperature favouring the production of grey pig. Mr. Bell has shown, indeed, that white pig-iron may be converted into grey pig by exposing it to a very high temperature (*Journal of the Iron and Steel Institute*, Nov. 1871, p. 277).

It is generally admitted that the best pig-iron is made from the clay ironstones of the coal-measures. Now this pig-iron contains both silicon and phosphorus, and Mr. Riley finds, by analysis of various kinds of pig from which the best wrought iron is made, that their average composition approximates very closely to that of the pig made from clay band ironstone. On the other hand, pig iron which is chemically very pure and nearly free from silicon and phosphorus, such as Swedish iron, yields very red-short wrought iron, and quite unfitted for the manufacture of wrought iron of the best quality, unless it be mixed with other kinds of pig-iron containing both silicon and phosphorus. These two elements appear therefore to play an important part in the manufacture of iron.

Silicon, when present in large amount, as in Bessemer pig, reduces the percentage of carbon; in inferior pig-iron containing much sulphur and phosphorus the percentage of carbon is always low.

4. *Condition of Carbon and Silicon in Pig-Iron.*—It is well known that in grey pig-iron the carbon exists in two states, *free* or *graphitic*, and *combined*, or in a state of intimate mixture. The graphitic particles are much lighter and more friable than the iron, and may be separated by pulverisation, sifting, and levigation: in many instances also they may be picked out with the point of a knife. The following determinations of the proportions of free and 'combined' carbon in two kinds of pig-iron and in the lighter portions separated by sifting and levigation, have been made by G. Snelus (*Journal of the Iron and Steel Institute*, Feb. 1871, p. 28):—

	Original pig	Siftings	Levigated powder
Bessemer pig { Graphite . . . . .	3.19	7.79	21.27
{ Combined Carbon . . . . .	0.20	0.17	—
Middlesborough forge pig { Graphite . . . . .	2.65	7.015	41.320
{ Combined Carbon . . . . .	0.35	0.3	—

Snelus is of opinion that the absorption of carbon by iron is rather a case of solution than of definite chemical combination.

Silicon invariably occurs in pig-iron, and is never entirely absent even in steel and wrought iron. In good Bessemer and in tool-steel it rarely exceeds 2 or 3 pts. in 10,000. The following results were obtained by the methods above mentioned:—

*Amount of Silicon per cent. in—*

	1 Original pig	2 Fine siftings	3 Levigated powder
West Cumberland Bessemer pig . . . . .	2.419	2.380	—
Dowlais Bessemer pig . . . . .	3.849	3.639	3.158
Middlesborough pig . . . . .	1.815	1.610	1.219

Here the silicon, unlike the graphite, does not increase in the finer portions, but diminishes. It remains with the iron just as the 'combined' carbon does. Hence Snelus concludes that the silicon is in combination or in solution in the iron, and is ever—except perhaps in an exceptional case—found in the free state.

Rammelsberg (*Deut. Chem. Ges. Ber.* v. 430) observed in the fracture of a rail white cast-iron roller from the 'Heinrichshütte' near Hattingen on the Ruhr, aggregations of regular octohedrons, which gave the following results by analysis:—

Graphite	Carbon	Silicon	Sulphur	Phosphorus
1·121	1·963	1·537	0·113	0·041,

the number of atoms of these elements and those of iron being in the ratio of 1 : 7·6, whilst in the crystallised iron from Gleiwitz, the ratio is 1 : 7·9; in that from Loelling, in Carinthia, 1 : 12; in that from Rothelhütte on the Hartz, 1 : 19; and in iron from Lauchhammer, 1 : 21.

This seems to be a confirmation of the view of Snelus (p. 695), also previously announced by Rammelsberg, that cast iron does not form definite compounds with carbon, but is a mixture of the isomorphous elements, iron, carbon, silicon, and phosphorus.

Another white cast iron which had been very slowly cooled under slag was also crystallised, but not so distinctly as the other, and showed the peculiar netted appearance often seen in substances crystallising in the regular system. It contained—

Carbon	Silicon	Phosphorus	Sulphur
2·820	0·334	0·086	0,

but only a trace of graphite. According to Karsten, white cast iron contains no graphite at all; but this is not correct. Bromeis a. Rammelsberg found that 'spiegeleisen' from Maegdesprung contains 16·5 p.c., and that from Lohhütte 28 p.c. of the total amount of carbon in the form of graphite.

5. *Cast Iron rich in Silicon*.—The variety of cast iron technically called 'glazed pig,' generally contains from  $1\frac{1}{2}$  to  $2\frac{1}{2}$  p.c. silicon, sometimes as much as 7·8 p.c. Its fractured surface is smooth to the touch, and brighter as the proportion of silicon is greater. Its production requires a very hot blast and a flux containing a considerable proportion of silica and alumina. The proportion of lime in the flux must not be too great, or the silica will combine with it. The use of the alumina appears to be to play the part of an acid in combining with the lime. A charge of 1,250 kilos. of ore containing 30 p.c. iron, with 100 kilos. coke and 800 kilos. flux consisting of 50 p.c. silica, 33 lime, 16 alumina, and 1 manganous oxide (the ratio of the oxygen in the silica to that in the bases being as 26 : 17·6) yielded a very fluid casting containing 7·90 p.c. silicon, 0·72 phosphorus, and 2·60 carbon (S. Jordan, *Compt. rend.* lxxvi. 1086).

The necessity for a very hot blast in the production of this variety of cast iron is accounted for by the fact that the oxidation of silicon evolves a large quantity of heat, and that consequently an equally large quantity will be required for the reduction of silica to silicon (p. 637). According to Troost a. Hautefeuille, 1 gram of silicon burning in oxygen to silica gives out 7,830 units of heat (p. 617); that is to say, more than twice as much heat as carbon evolves in burning to carbonic anhydride; and if, as often happens in metallurgic processes, the carbon burns only to monoxide, it gives off about three times less heat than an equal weight of silicon burning to silica.

Cast iron rich in silicon (7 to 8 p.c.), heated in a lime crucible under a flame of coal-gas and oxygen, refines quite quietly without sparkling, the surface of the metal-bath becoming covered with an iridescent film, which is continually being thrust to the sides of the vessel and replaced by a new coating. The refining of iron rich in carbon, on the contrary, is attended with vivid sparkling. The cause of this appears to be that the carbon burns to monoxide, and this gas at the high temperature of the fused metal is absorbed by it and given up again in the cooler parts of the bath, carrying with it small white-hot particles of iron which appear as sparks. Silicon, according to Caron's observations, decomposes carbon monoxide, which, therefore, in presence of silicon, cannot act in the manner just explained. Its action in preventing the formation of sparks may be immediately neutralised by adding a certain quantity of manganiferous cast iron, which quickly removes the silicon (Troost a. Hautefeuille, *Compt. rend.* lxx. 262).

By fusing red hæmatite with sand and charcoal, Riley has succeeded in preparing a silicide of iron containing as much as 21·7 p.c. silicon. This compound is quite insoluble in hydrochloric acid, and dissolves but slightly in aqua regia, even after long boiling (*Chem. Soc. J.* [2], x. 549).

\* *Copper in Iron*.—According to C. Rump (*Arch. Pharm.* [2], cxlv. 231) the purest iron of commerce is not free from copper. This is especially the case in iron smelted with coke, since coke always contains iron pyrites, and the latter always contains copper. In one case 100 grams of iron yielded 0·1 gram copper; two samples of Swedish iron (cast and wrought) and two kinds of Hartz pig (smelted with charcoal) contained only traces of copper.

6. *Malleable Cast Iron*.—The difficultly fusible pig-iron smelted with charcoal at Ulverstone in Lancashire may be rendered malleable by melting it in crucibles,



casting it, and then heating the very hard metal in cast-iron crucibles with pulverised quartziferous red hematite in such a manner that a bright red heat may be attained in 24 hours. This temperature is kept up for three to five days. For thick pieces, which are afterwards to be bored, the heating must be several times repeated. The metal thus obtained is very much like good wrought iron; its density is that of cast iron; colour somewhat lighter than that of wrought iron; fracture mostly white and fine-grained; pieces more than 8 to 10 mm. thick have an external zone of wrought iron with a nucleus of cast iron: thick pieces cannot, therefore, be welded. According to Weddington, the metal to be made into malleable cast iron must be as free as possible from silicon, phosphorus, and sulphur. The method above described is best adapted for castings which are to retain their exact form after being rendered malleable; but for metal which is afterwards to be shaped by forging, a simpler method of preparation is to melt pig-iron with bar-iron (*Dingl. pol. J. exv. 281*).

Poulet, Nagant and Co. prepare malleable cast iron by immersing the castings in a bath of easily fusible slag rich in iron (*Génie industriel*, 1870, Mars, 148).

**II. Wrought Iron.** 1. *Preparation of Pig-Iron for the Puddling process.*—J. P. Budd (*Dingl. pol. J. exvi. 479*) describes a method of preparation intended chiefly to diminish the proportion of silicon in pig-iron. For this purpose the iron is run from the blast-furnace into moulds, on the sides of which a paste of ground hematite and water (sometimes with addition of Chile saltpetre) has been dried. The metal, when run into these moulds to the depth of  $3\frac{1}{2}$  to 4 inches, boils up strongly, gives out flames (? burning silicon), and a coating of slag is formed on the surface of the purified cast iron. By this process the amount of silicon in white pig-iron may be reduced from 1 to 0.002–0.003 p.c. without perceptibly altering the proportion of carbon. Pig-iron thus prepared is very easily puddled.

P. Tunnor (*Dingl. pol. J. cci. 245*) describes Henderson's process, much used in North America, for removing phosphorus from pig-iron. The mould into which the iron is run from the blast-furnace is filled to the depth of  $\frac{1}{4}$  to  $\frac{3}{8}$  of an inch with a mixture of 1 part by weight of fluorspar and 2 parts of iron ore (red hematite or roasted spathic iron ore), which is so finely pounded as to pass through a sieve of 400 meshes to the square inch. The iron is run from the furnace in quantity sufficient to form a layer an inch deep in the mould. By the high temperature of the iron, fluorine and oxygen are said to be liberated from the mixture, and thereby the silicon and phosphorus are volatilised. A pig-iron containing 2.3096 p.c. silicon and 0.4196 p.c. phosphorus yielded by this process a refined iron containing no silicon and only 0.1029 p.c. phosphorus. The bar iron prepared from it contained only 0.0087 p.c. phosphorus.

*Removal of Phosphoric Acid from Iron Ores.*—This may be effected by treating the ores with sulphurous acid either gaseous or in aqueous solution. The phosphoric acid is then washed out with water and neutralised with lime, whereby a calcium phosphate is obtained fit for use in agriculture. The ores thus purified yield pig-iron free from phosphorus (*J. Jacobi, Dingl. pol. J. cci. 245*).

2. *Machine Puddling.*—Several attempts have been made to puddle iron by machinery, and for some time past mechanical rabbles have been attached to puddling furnaces to assist the workmen in the heavy labour of stirring the iron; their use has not, however, been very extensive, and they are useless for the purpose of bolting up the iron, which is one of the most laborious parts of puddling.

Various inventors have used a revolving chamber so as to puddle the iron mechanically, but with only partial success, the chief difficulty having been to obtain a suitable lining for the chamber. The problem has, however, at length been successfully solved by Mr. Dankes, whose rotatory puddling furnace has for some time past been used in America.

Mr. Dankes' machine consists of a revolving cylindrical chamber, made with longitudinal wedge-shaped recesses, which act mechanically in retaining the initial lining in its place. This initial lining may be composed of any ore free from silica, ground up and mixed with lime-cream; it is put in like mortar, and, when dried, becomes a refractory and sufficiently coherent material to allow of the inner lining, or fettling, being melted upon it without either melting itself or breaking away from the plates. It is advisable to use an anhydrous ore for mixing with the lime, as when a hydrate is used and the water of combination driven off, the mixture becomes rather crumbly.

Upon the initial lining a quantity of any ore free from silica is melted. For this purpose ores containing water of combination may be used, as it is soon driven off. Into the melted bath of ore large solid lumps are thrown, and these being cold, cause the melted ore to set round them, and so fix them firmly, producing a rough internal lining, and thereby affording a greater amount of surface to act upon the iron. It is not only necessary that these lumps shall be moderately free from silica, and refrac-

tory, but also that their texture shall be such that they do not crumble by heat; this was found to be the case with ilmenite.

Best tap-cinder answers for this purpose very well, and when iron ores cannot be got free from cinder, there is no doubt that iron scrap may be profitably oxidised for the purpose: Mr. Dankes, indeed, uses scrap iron for this purpose.

The furnace is provided with a closed ash-pit, and the necessary air is supplied by a fan-blast; nine jets of air are introduced over the fire grate in front of the furnace and above the fuel, so that the puddler in charge of the machine can regulate the blast, and increase the heat when required.

This furnace is a bad melter of pig-iron, as it takes a long time and consumes much fuel in using the machine. The pig should be melted in a cupola, or run direct from the blast-furnace.

After melting the iron, a jet of water is directed against the lining on the descending side, in order to chill a portion of the cinder and cause it to be carried under the iron. This appears also to have the effect of carrying off sulphur from the cinder.

When grey pigs are used, it takes about ten minutes for the boil to commence; with white pig the time is much less, on account of the silicon present in the iron being less, and the boil commences in two minutes after melting. After tapping off the cinder, the cylinder is set revolving, and the fire is urged; the iron begins to boil violently, and the carbon quickly disappears. But little cinder is formed in this part of the process, and most of it is removed with the ball.

The removal of the iron from the chamber is effected by an ingenious arrangement consisting of a moveable piece or door at the back of the flue; this, on removal, permits the ball to be withdrawn by means of a ball fork worked with a crane, by which the ball is placed on a bogie and carried to the squeezer or hammer.

In Mr. Dankes' machine the puddling is effected entirely by the fettling, the carbon, silicon, and phosphorus being oxidized almost entirely by it and the cinder introduced. The separation of the silicon, sulphur, and phosphorus by this puddling machine is more perfect than by hand puddling.

Moreover, the impurities in the pig being oxidized at the expense of the fettling and cinder, the oxides of iron must be converted into metallic iron, and consequently the yield is increased; thus 21·602 lbs. of pig gave of puddle-bar 23·112 lbs., allowing 94 p.c. for the iron in the pig, and 1·652 lb. of iron was reduced from the fettling.

The present machinery in use at iron works is quite unfitted for dealing with such a mass of iron as a ball from Dankes' furnace; the charge used being 600 lbs., the puddle ball would weigh about 650 lbs. Mr. Dankes has invented a squeezer suitable for such masses of iron, consisting of an eccentric grooved roller, with two smaller ones, and a cam to tumble up the iron laterally.

Iron thus produced, after being thoroughly squeezed and re-heated, can be rolled out at once into a rail or large bar, and will not require, as is the case at present, rolling into puddle-bar, piling, re-heating, and rolling again.

Mr. Spencer, of the West Hartlepool ironworks, has also invented a revolving puddling machine. The converter is of a rhomboidal form on two of its opposite sides, having the axes at right angles with the ends or discs, the remaining two sides being parallel to the axis; the ends or discs are made to revolve on rollers by suitable gearing. The sides are fitted with honeycomb recesses to hold the fettling, the discs being honeycombed also for the same purpose.

The fettling used is best tap; it is fitted into the recesses, and fresh tap is melted over it. In some experiments made by Mr. Spencer, the silicon and phosphorus were found to be almost completely separated; from some Cleveland pig containing over 2 p.c. of phosphorus this element was reduced in the puddle-bar to less than ·10, and some of this was probably due to the cinder in the puddle-bar (Riley, *Chem. Soc. J.* [2], x. 557).

III. **Steel.** 1. *Manufacture from Pig-Iron.*—A new method of obtaining steel from pig-iron has been invented by A. Berard (*Dingl. polyt. J.* cc. 470). The fuel used is gas, obtained by passing over-heated steam through a layer of red-hot coke, the gaseous mixture thus produced being rich in hydrogen and carbon monoxide, poor in nitrogen, free from carbon dioxide, and capable of producing a very high temperature. By regulating the draught over the surface of the heated metal, either a reduction or an oxidising action may be obtained. The pig-iron is run direct from the blast-furnace, or from a cupola-furnace, on to a hearth capable of containing from 5,000 to 6,000 kilograms. By alternate treatment with the oxidising and the reducing flame the iron is freed from silicon, phosphorus, &c., with very little loss by oxidation. Spiegeleisen melted on a neighbouring hearth round which the heated gases circulate as they pass off, may be added to the iron on the principal hearth in proportions determined by the kind of steel required. The waste heat of the furnace may be utilized for heating the gases and the air by which they are to be burnt.

2. *Comparison of Bessemer and Heaton Steel.*—The two methods of manufacture are alike in this respect, that the refining agents are brought into much more intimate contact with the iron than was possible in the old puddling process. The Bessemer process requires the use of purer pig-iron than that of Heaton. Bessemer effects the oxidation by means of various oxides of iron; Heaton by the use of salt-petro, which is dearer. The greater costliness of Heaton's method is, however, partly compensated by the lower price of the less pure pig-iron which can be used in it (C. Schinz, *Dingl. pol. J.* cxcv. 126).

3. *Use of Ferromanganese or Spiegeleisen in the Manufacture of Steel.*—Alloys of iron and manganese are extensively used in the manufacture of steel. W. Henderson in Glasgow prepares them by reducing a mixture of ferrous oxide and manganoan carbonate on the hearth of a Siemens' furnace, and fusing the spongy mass to a regulus under a reducing flame. It does not appear possible to obtain all the manganese of the charge in the metallic state, a slag rich in manganese being obtained which may be utilised in subsequent operations. At the works of the Torre noire, in Voulte and Besièges Company in France, iron alloys containing 23-25 p.c. manganese are prepared by Henderson's process, and used for the manufacture of steel. The pig-iron is worked direct from the blast-furnace, and the re-heating and sorting are avoided by the use of large quantities of manganese alloys. The steel produced is soft and specially available for the manufacture of boiler-plates, armour-plates for ships, &c. From experiments by W. Fairbairn it appears that this steel is inferior to the best sorts in tenacity, but that this deficiency is compensated by greater extensibility and malleability. It appears to be particularly well adapted for wire-making (F. Kohn, *Dingl. pol. J.* cxviii. 205; cc. 280).

4. *Gases evolved in the Bessemer Process.*—The gases evolved from the converter at various stages of the process have been examined by G. Snelus (*ibid.* cxii. 145). A fire-proof tube was sunk into the converter deep enough to prevent the access of the external air; and the gas given off was passed through an iron tube into glass tubes in which the quantities required for analysis could be sealed up. The results of the analyses are given in the following table:—

	I. 2 min.	II. 4 min.	III. 6 min.	IV. 10 min.	V. 12 min.	VI. 14 min. after the beginning of the blast
CO <sup>2</sup>	10.71	8.57	8.20	3.58	2.30	1.34
O	0.92	—	—	—	—	—
CO	—	3.95	4.52	19.59	20.30	31.11
H	88.37	0.88	2.00	2.00	2.16	2.00
N		88.58	85.28	74.83	66.24	65.55
Hydrocarbons	—	—	—	—	—	—

The accompanying spectra exhibited the following characters:—

I. Continuous Spectrum	II. Sodium line	III. Sodium Potassium Lithium lines	IV. Complete Spectrum with Carbon lines	V. Complete Spectrum	VI.
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These analyses show that at the commencement of the blast, nothing but carbon dioxide is formed, afterwards chiefly carbon monoxide, but no hydrocarbons. Snelus is of opinion that this proportion is independent of the temperature, which is lower at the beginning of the blast than afterwards. Alteration of the temperature produces alteration of the spectrum. Observations on these results have been made by W. M. Williams (*Chem. News*, xxiv. 174), and J. Parry (*ibid.* 203). Roscoe (*Chem. News*, xxiii. 174, 182) gives the following results of observation of the Bessemer flame with the naked eye and with the spectroscope:—

Time in Minutes	Naked Eye	Spectroscope
First stage 0 to 4	Small flame visible	Faint continuous spectrum, with sparks proceeding from ignited metal
4 to 6	Small pointed flame	Bright spectrum with flashes of the sodium line
6 to 8	Unsteady flame with explosions	Spectrum bright, sodium line permanent, red lithium and potassium lines
Second stage 8 to 10	Bright dense flame	Besides the lines above mentioned, bright carbon lines* appear in the red, green, and blue
10 to 14	Flame bright in the lower part, but less dense	The green carbon lines brighter than before
Third stage 14 to 16	Flame less bright and smaller	The carbon lines in the green become indistinct
16 to 18	The flame disappears: blast discontinued	The bright carbon lines in the green disappear suddenly. Spectrum continuous

The observations of the alterations in the flame afford the means of ascertaining the precise moment at which the blast should be discontinued.

Similar observations on the spectroscopic appearances of the Bessemer flame have been made by J. M. Silliman (*Sill. Am. J.* [2], v. 297; *Chem. News*, xxii. 313; xxiii. 5), who has also studied the colours of the flame when viewed at different stages of the process through yellow and blue glasses. He points out that both the colours thus seen, and the lines in the spectrum, disappear in the reverse order to that in which they were developed. The similarity of the appearance of the flame and its spectrum in the last stage to that which it exhibited at the beginning is the characteristic indication of the termination of the process. The colours and lines disappear much faster than they appear.

**5. Phosphoretted Steel.**—The properties of phosphoretted steel have been examined by L. Gruner (*Compt. rend.* lxx. 571), with the following results:—1. Phosphorus to the amount of 2 or 3 parts in a thousand renders steel strong and elastic. It increases the elasticity and extensibility without altering the hardness. Steel of this kind, however, is deficient in tenacity, and is brittle without being hard. 2. To judge of this want of tenacity, it is not sufficient to submit the steel to a longitudinal stretch or to transverse pressure, but it must be subjected to the action of a blow or a thrust. 3. The quantity of saltpetre employed in Heaton's process is not sufficient to remove the whole of the phosphorus.

**6. Burnt Iron and Steel.**—This term is applied to iron which has been damaged by re-heating, or by being excessively heated and exposed in the puddling furnace balling.

Burnt iron is brittle, it displays the so-called crystalline structure, and has lost the fibrous structure and silky fracture of good iron. When steel has been raised to a yellow or white heat, and then suddenly cooled, it becomes brittle, and no longer capable of tempering, and is worthless for the ordinary uses of steel until again raised to a welding heat, rolled or hammered, and allowed to cool gradually. Burnt steel has a coarse granular fracture, the facets of the granules being, for the most part, either rounded or conchoidal.

W. M. Williams (*Chem. Soc. J.* [2], ix. 700) infers, from the examination of a large number of samples of burnt iron and steel, that the burnt iron is penetrated throughout by ferric oxide, and that burnt steel is much poorer in carbon than ordinary steel. He attributes the change in both cases to the absorption of oxygen by the heated metal, giving rise in the one case to ferric oxide, in the other to carbon monoxide. When such steel, still containing carbonic oxide, is quickly cooled, some of the bubbles of gas may be retained, giving rise to the cavities called 'toad's eyes.' W. H. Johnson

\* Dr. W. M. Watts has lately shown that the lines in this spectrum, formerly supposed to be carbon lines, are really due to the presence of an oxide of manganese (see *Spectral Analysis*).

(*Chem. News*, xxiv. 250) considers that the oxidation taking place in the interior of a mass of iron is due, not to free oxygen, but to carbon dioxide, which is always present in the furnaces together with monoxide; if the dioxide predominates, oxidation may take place, but in presence of excess of carbon monoxide the burning of the iron is impossible. Riley (*Chem. Soc. J.* [2], x. 561) failed to discover the presence of oxide in burnt iron, and thinks that the change in burnt iron is more probably due to the particles of iron becoming soft enough to arrange themselves in a highly crystalline form, and that possibly some gas may remain between the interstices of the crystals. Brittle iron may be rendered fibrous by mechanical working, and fibrous bar iron may be made red-short by fusion. In considering the quality of wrought iron and steel, it is therefore necessary to look to the mechanical treatment to which it has been submitted, as well as to its chemical composition.

II. Caron (*Compt. rend.* lxxiv. 662) finds that good fibrous wrought iron, whether heated in the furnace of an ordinary forge, or in a porcelain tube through which nitrogen or hydrogen is passed, has a crystalline structure after cooling. All the pieces thus treated, when forged at a red heat or broken cold, exhibited the same qualities and the same defects, and all were restored to their primitive state by heating to whiteness. Since then burnt iron is obtained by heating iron in a reducing as well as in an oxidising atmosphere, its properties cannot well be attributed to oxidation, but appear rather to be due to a modification of its molecular structure by heat.

7. *Spitting of Steel*.—The following explanation of the spitting of steel during solidification is given by Caron (*Compt. rend.* lxx. 451, 453, 1263). Even in a reducing flame containing a large proportion of hydrogen, iron is oxidised by the water contained in the flame, and the ferric oxide thus produced reacts with the carbide of iron in such a manner as to produce carbon monoxide. This gas, developed during the fusion in the interior of the mass, breaks through the thin solid layer of metal, and thus produces the spitting. The carbon oxide is not absorbed by the iron during fusion and given off again on solidification, but is continually evolved during the fusion. The same phenomena take place even when every trace of excess of oxygen is prevented from coming in contact with the metal, by the use of lime dishes instead of porous crucibles. The fused ferric oxide in the lime dish likewise exhibits the phenomena of spitting on cooling. Ferric oxide can, therefore, absorb gases during fusion and give them off again on cooling. The nature of these gases has not yet been determined, but the spitting of steel is perhaps due to the thin layer of oxide formed during the fusion.

IV. *Preparation of Malleable Iron and Steel direct from the Ore*. In the 1st *Suppl.* p. 756, a description is given of Siemens' method of obtaining malleable iron and steel direct from the ore, by feeding the ores (oxides) mixed with carbonaceous materials into a reverberatory furnace through hoppers of fire-clay, the intention being to effect the reduction of the ores into spongy metal during their descent, and the fusion of the spongy metal so produced, on the open hearth of the furnace, pig-metal being used to facilitate the fusion. It was found, however, that the quantity of heat which had to be transmitted through the sides of the fire-clay hopper was so great, that the process of reduction proceeded very slowly, and the hoppers themselves were rapidly destroyed by the intense heat of the furnace. The reduction of the metallic iron in closed chambers of this or any other form which has been tried cannot be effected in less than about 36 hours, and that at a great expenditure of fuel for heating the chamber externally.

This unsatisfactory result led to the adoption of another method of producing spongy iron by means of a rotative furnace. This furnace consisted of a long cylindrical tube of iron of about 8 feet diameter, mounted upon antifriction rollers; the brick lining of it was provided with longitudinal passages for heating currents of air and gas, prior to their combustion at the one extremity of the rotating chamber. The flame produced passed thence to the opposite or chimney end, where a mixture of crushed ore and carbonaceous material was introduced. By the slow rotation of this furnace the mixture advanced continually to the hotter end of the chamber, and was gradually reduced to spongy iron. This dropped through a passage constructed of refractory material on to the hearth of a steel-melting furnace, where a bath of fluid pig-metal had been provided. The supply of reduced ore was continued till the carbon in the mixture was reduced to the minimum point. The rotation was then arrested to prevent further descent of reduced ore; spiegeleisen was added; and the contents of the melting furnace tapped into a ladle and thence into ingots.

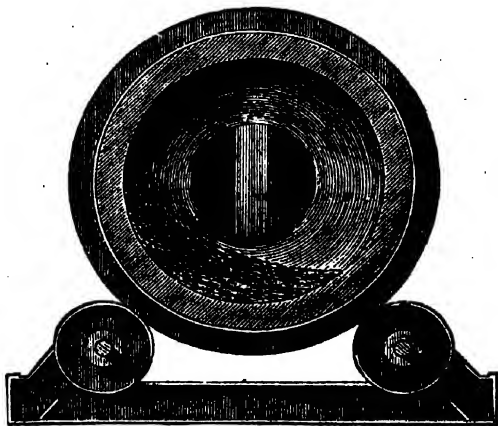
This rotatory furnace was erected at the Landore Works in Sheffield in 1869, and it was so far successful, that the reduction of the ore was accomplished in a comparatively short time. A difficulty, however, presented itself, which led to its immediate abandonment; it was found that the spongy metal produced absorbed sulphur from

the heating gases, and was rendered unfit for the production of steel; the spongy iron, moreover, upon its introduction into the steel-melting furnace, floated upon the metallic bath without being readily absorbed into it, and was in great part reoxidised and converted into slag by the action of the flame in the furnace.

These experiments showed that the successful application of reduced ores could not be accomplished through their conversion into spongy metal. On the other hand, it had been observed that in melting iron ores no sulphur is absorbed from the flame; and it was ultimately found that by melting ores mixed with fluxing materials in a furnace so arranged as to accomplish its fusion in a continuous manner, and on a large scale, the fused ore might be acted upon by solid carbonaceous matter, so as to separate the metallic iron in a more compact form, while the earthy constituents of the ore would form a fusible slag with the fluxing material. Experiments proved that this reduction by precipitation of the iron could be accomplished only at an intense heat, exceeding the welding heat of iron, but that the iron so produced was almost chemically pure, although the ores and the fuel used might contain a very considerable percentage of sulphur and phosphorus.

The rotatory furnace in which the smelting is performed consists of a set of four regenerators, of the construction shown in the 1st *Suppl.* (p. 756). The rotative chamber, a vertical section of which is shown in figure 17, is constructed of iron, and rests upon four anti-friction rollers. Wheel-gearing is applied by which either a very slow rotative velocity of from four to five revolutions per hour can be imparted to the chamber, or a more rapid velocity of about 60 to 80 revolutions per hour. The chamber is about 7' 6" in diameter and 9' 0" long, and is provided with a very refractory lining made of bauxite mixed with about 3 p.c. of clay, or water-glass, and 6 p.c. plumbago (p. 126).

FIG. 17.



A tap-hole is placed on the working side for discharging the slag into a cove below, where it is received in vessels mounted on wheels. At the two extremities of the cylindrical rotative chamber with its truncated ends, are large orifices, one of which, on the side of the regenerators, serves for the introduction of the heated gas and air, as well as for the exit of the products of combustion, and the other, facing the working platform, is closed by a stationary door hung before it in the usual manner.

This rotative furnace is worked as follows:—

The ore to be smelted is broken up into fragments not exceeding the size of peas or beans; to it is added lime or other fluxing material, in such proportion that the gangue contained in the ore and flux combines with only a little protoxide of iron into basic and fluid slag. If the ore is hæmatite, or contains silica, it is best to add alumina in the shape of aluminous iron ore; manganiferous iron ore may also be added with advantage. A charge of about 20 cwts. of ore is put into the furnace when fully heated, while it is slowly revolving. In about forty minutes this charge of ore and fluxing material will have been heated to bright redness, and at this time from 5 cwts. to 6 cwts. of small coal of uniform size (not larger than nuts) are added to the charge, whilst the rotative velocity is increased in order to accelerate the mixture of coal and ore. A rapid reaction is the result: the ferric oxide being reduced to magnetic oxide

begins to fuse, and at the same time metallic iron is precipitated by each piece of carbon, while the fluxing materials form a fluid slag with the siliceous gangue of the ore. The slow rotative action is again resorted to, whereby the mass is turned over and over, presenting continually new surfaces to the heated lining and to the flame within the rotator.

During the time of this reaction, carbonic oxide gas is evolved from the mixture of ore and carbon, and heated air only is introduced from the regenerator to effect its combustion within the rotating chamber. The gas from the gas-producers is entirely or almost entirely, shut off during this portion of the process. When the reduction of the iron ore is thus nearly completed, the rotator is stopped in the proper position for tapping off the fluid cinder; after this the quick speed is imparted to the rotator, whereby the loose masses of iron contained in it are rapidly collected into two or three metallic balls. These are taken out and shingled in the usual way of consolidating puddled balls; the furnace is tapped again, and is ready to receive another charge of ore. The time occupied in working one charge rarely exceeds two hours; and supposing that 10 cwt. of metallic iron is got out per charge, the apparatus is capable of turning out at least 5 tons of puddled bar per diem. If anthracite or hard coke is available for effecting the reduction of the ore, it should be crushed much finer than when coal or brown coal is used, the idea being that each particle of the reducing agent should be fully consumed during the period of chemical reaction. If wood is used, it has to be charged for the same reason in still larger pieces.

If it is not intended to make iron, but cast steel, the balls may be transferred from the rotator to the bath of a steel-melting furnace in their heated condition, and without subjecting them to previous consolidation under a hammer or shingling machine.

It is feasible, however, to push the operation within the rotator to the point of obtaining cast steel. If this is intended, the relative amount of carbonaceous matter is somewhat increased in the first instance, so that the ball, if shingled, would be of the nature of puddled steel, or contain even some carbon mechanically enclosed.

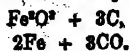
If now, after removing the cinder by tapping, from 10 to 15 p.c. of ferro-manganese or spiegeleisen is thrown in, and the heat within the rotator is rapidly raised by urging the influx of heated gas and air from the regenerator, the metallic balls will soon be seen to diminish, and presently a metallic bath only will be found in the furnace, which may be tapped into moulds and hammered and rolled into steel blooms or bars in the usual manner. Experience alone can determine which mode of working will ultimately prove the best; but it is probable that, for the production of cast steel on a large scale, it will always be more profitable to transfer the metallic balls to a separate melting furnace, a series of rotating furnaces working in concert with a series of steel-melting furnaces, to produce charges of 5 to 6 tons of fluid steel.

In comparing upon theoretical grounds this method of producing metallic iron with the operation of the blast-furnace, it will be at once perceived that, whereas in the blast-furnace the products of combustion consist chiefly of carbon monoxide, and issue from the top of the furnace at a temperature exceeding  $350^{\circ}$ , the result of combustion in the rotative furnace is carbon dioxide, which issues from the regenerative furnace into the chimney at a temperature rarely exceeding  $175^{\circ}$ . This proves at once a great possible saving of fuel in favour of the proposed method, and to this saving has to be added the fuel required in converting pig-metal into wrought iron by the puddling process.

It may, however, be asked why the rotating furnace should admit of the complete combustion of carbon, whereas in the blast-furnace such complete combustion is, as is well known, not possible, because each atom of carbon dioxide formed would immediately split up into two atoms of carbon monoxide by taking up another atom of carbon from the coke present. The following explanation will serve to elucidate this point:

In the rotative furnace streams of carbon monoxide are set up within the mass under reaction; and this gas on reaching the surface meets the current of intensely heated air proceeding from the regenerators, and effects with it perfect combustion within the free space of the chamber. The carbon dioxide thus generated comes into no further contact with carbon; consequently, it cannot be split up, but is drawn away unchanged into the chimney, while the evolved heat is taken up by the sides of the chamber, and transmitted by reverberation and conduction to the mixture of ore, fluxes, and coal.

In this process there are, therefore, two things to be accomplished, viz., the deoxidation of the ore, and the fusion of the earthy matter mixed with it. Taking, for example, hematite ore, consisting of ferric oxide with 10 p.c. of silica, the quantity of carbon necessary for its reduction will be determined by the formula



which gives

According to this formula, the consumption of carbon (taking its atomic weight at 12 and that of iron at 56) amounts to:

$$\frac{3 \times 12}{9 \times 56} = 0.32 \text{ lb. per lb. of iron reduced.}$$

The heat absorbed in this reaction amounts, according to Debus, to 892 units per lb. of iron produced; but, on the other hand, the further combustion of 0.32 lb. of carbon from the condition of CO to that of CO<sup>2</sup> by means of the free oxygen introduced into the rotative chamber from the regenerator, yields:

$$0.32 \times 5,600 = 1,792 \text{ units of heat,}$$

leaving  $1,792 - 892 = 900$  units

available for heating the materials and for melting the slag.

The quantity of materials to be heated per lb. of iron produced would amount to—

Ore	.	.	.	.	.	1.59
Lime or other fluxing materials	.	.	.	.	.	0.16
Total	.	.	.	.	.	1.75

and taking the specific heat of Fe<sup>2</sup>O<sup>3</sup> as 0.154, as determined by Kopp, and the temperature to which the materials have to be raised as 1,500° C., the heat required for this purpose would not exceed

$$1.75 \times 0.154 \times 1,500 = 404.5 \text{ units.}$$

To this consumption would have to be added the latent heat absorbed in liquefying the slag. The slag would amount to 0.16 lb. silica and 0.16 lb. lime = 0.32 lb. per lb. of iron produced; and, although we have no precise data from which to ascertain the latent heat absorbed in liquefaction, we can hardly estimate it at more than 150 units per lb., or at  $0.32 \times 150 = 48$  units, which, with the above 404.5, makes 452.5 units, or 447.5 units under the 900 heat-units which are available, proving that 0.32 lb. of pure carbon would, theoretically speaking, amply suffice to produce 1 lb. of puddled bar from ordinary hematite ore, without counting, however, losses of heat by radiation and from other causes.

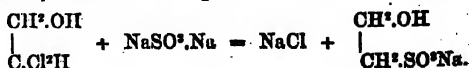
In the production of cast steel three operations are essentially involved, viz.: the deoxidation of the iron, the fusion of the slags, and the fusion of the metal itself with such proportion of carbon and manganese as is necessary to constitute steel of the temper required.

The theoretical quantity of fuel required to accomplish these operations would exceed that of making wrought iron, by the fusion of heated metal, which may be estimated at about 1,000 units, or at  $\frac{1,000}{8,000} = 1.25$  lb. of carbon per lb. of steel produced, which have to be added to the 0.32 lb. used in reduction. In fine, a ton of iron ought to be producible from hematite ore with 6.4 cwts. of carbonaceous matter, or about 8 cwts. of common coal, and a ton of cast steel with 8.91 cwts. of carbon or say 11 cwts. of coal.

These figures may never be completely realised; indeed, taking incidental losses by radiation, through imperfect combustion, and through imperfect absorption of heat, into account, we find that the actual consumption exceeds the theoretical limits about three times, or that a ton of iron can practically be produced with a consumption of 25 cwts. of coal, and a ton of cast steel with 40 cwts. of coal; but this consumption still represents a great reduction as compared with other methods of production. (Siemens, *Chem. Soc. J.* [2] xi. 662-678.)

**ISATIN.** On the constitutional formula of this body and its reduction to indigo-blue, see Indigo (p. 666).

**ISETHIONIC ACID.** *Oxethylsulphonic acid*, C<sup>2</sup>H<sup>5</sup>SO<sup>3</sup> = CH<sup>3</sup>OH.CH<sup>2</sup>SO<sup>3</sup>H.—The sodium salt of this acid is formed by heating the hydrochloride of ethylene oxide (ethylene-chlorhydrin) with sodium sulphite to 170°–180° in sealed tubes:



The evaporated solution treated with boiling alcohol yields sodium isethionate, from which the pure acid may be obtained by treatment with sulphuric acid, evaporation, exhaustion with alcohol, saturation with barium carbonate, and decomposition of the resulting salt with sulphuric acid (A. Collmann, *Ann. Ch. Pharm.* cxlviii. 191).



**Ammonium Isethionate**,  $\text{CH}^2\text{OH}.\text{CH}^2\text{SO}^-\text{NH}^+$ , melts, according to Strecker, at  $130^\circ$ , and when heated to  $210^\circ$  gives off water and is converted into taurine,  $\text{C}^2\text{H}^4\text{NSO}^2$  (r. 609). H. Seyberth, on the other hand, states that it melts at  $135^\circ$ , is not altered by heating to  $210^\circ$ – $230^\circ$  for several days, but when heated to  $230^\circ$ – $240^\circ$ , is decomposed with frothing, and converted into isethionamide  $\text{CH}^2\text{OH}.\text{CH}^2\text{SO}^-\text{NH}^2$ , isomeric with taurine (*Deut. Chem. Ges. Ber.* vii. 391).

**Homologues of Isethionic Acid.**—**Amyl-isethionic acid**,  $\text{C}^2\text{H}^{12}\text{SO}^4 = \text{C}^4\text{H}^8\text{OH}.\text{CH}^2\text{SO}^-\text{H}$ , is formed by the action of sodium sulphite on amyleno-chlorhydrin (Falk), and by the action of sulphuric anhydride on amyl alcohol (E. Schwarz, p. 65).

**Methyl alcohol** is strongly attacked by sulphuric anhydride, but when the action is made to go on very slowly by pressing the anhydride into a narrow glass tube, and introducing this into a wider tube containing methyl alcohol, crystals form after a while, apparently consisting of methylene sulphite  $\text{CH}^2(\text{SO}^2)^2$ ; these, however, afterwards disappear, and the alcohol becomes more viscid; and if, after all the anhydride is absorbed, the liquid be diluted with water, boiled for some hours, saturated with barium carbonate, filtered, concentrated, mixed with alcohol, again filtered, and then left to stand over sulphuric acid, a hygroscopic crystalline mass is obtained, which may be purified by recrystallisation from dilute alcohol, and probably consists of barium methyl-isethionate. Similar results are obtained with *butyl alcohol* (Schwarz).

**Propyl-isethionic acid**,  $\text{C}^2\text{H}^{10}\text{SO}^4 = \text{C}^2\text{H}^4\text{OH}.\text{CH}^2\text{SO}^-\text{H}$ , is formed by the union of propylene oxide with the acid sulphite of an alkali-metal  $\text{C}^2\text{H}^4\text{O} + \text{HSO}^-\text{Na} = \text{C}^2\text{H}^4\text{OH}.\text{SO}^-\text{Na}$  (Erlenmeyer, *Ann. Ch. Pharm.* clviii. 260).

**ISOBIURET.** See BIURET (p. 193).

**ISOCLASE.** A basic calcium phosphate,  $4\text{CaO}.\text{P}_2\text{O}_5 + 5\text{H}_2\text{O}$ , said to come from Jochimssthal. Forms colourless triclinic crystals, having a specific gravity = 2.95, hardness = 1.5 (F. Sandberger, *J. pr. Chem.* [2], ii. 125).

**ISODINAPHTHYL.** See NAPHTHYL.

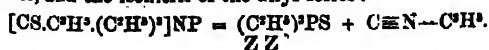
**ISOMORPHISM.** *Structure of Isomorphous Crystals.*—Kekulé (*Deut. Chem. Ges. Ber.* ii. 652), from an examination of the isomorphism of certain ferrous salts with magnesium or calcium salts, was led to infer that a like crystalline form does not necessarily imply a similarity of the molecules on all sides, but may be a consequence of partial similarity, and perhaps even of similarity on one side only of the molecules. This view is supported by certain observations made by H. Baumbauer (*ibid.* v. 859) on the form of the corrosion figures produced by the action of solvents on various isomorphous crystals. These corrosion figures are mostly microscopic hollows bounded by regular surfaces, the form of which evidently bears a certain relation to the general proportions of symmetry of the crystal. The figures produced on isomorphous crystals always exhibit a certain similarity of form, but have not always the same position relative to the surfaces of the crystal. Thus there is no important difference between the figures produced by water on the isomorphous members of the monoclinic group, including sulphate of iron, sulphate of iron and ammonium, sulphate of nickel and potassium, and sulphate of nickel and ammonium. The figures correspond in position, although the analogous surfaces of these bodies do not behave in exactly the same manner (which is in accordance with the slight differences of angle existing between them). In particular the figures on the two latter salts resemble each other very closely.

The group calcspar, dolomite, and spathic iron ore exhibits a contrary behaviour. Hydrochloric acid produces on the rhombohedral cleavage-planes of calcspar, hollows of the form of an isosceles triangle, with the apex towards the terminal summit of the crystal. Similar figures are produced by hydrochloric acid on the rhombohedral cleavage-planes of spathic iron ore, but in this case the base of the triangular hollow is towards the terminal summit of the crystal. According to Haushofer, dolomite behaves similarly to spathic iron ore.

The resemblance or difference in the position of the corrosion figures in these isomorphous bodies appears to point to a resemblance or difference in the structure or molecular form of the crystals.

**ISONITRILS, ISOCYANATES, or CARBIMIDES.** *Allyl-triethyl-sul-*

*phocarbophosphamide*,  $\text{N} \begin{Bmatrix} (\text{CS})^2 \\ \text{C}^2\text{H}^2 \\ (\text{C}^2\text{H}^2) \end{Bmatrix} \text{P}$ , formed by the union of allyl sulphocarbimide (volatile mustard-oil) with triethylphosphine (iv. 611), is resolved by heat into triethylphosphine sulphide, and the isonitril of the allyl series:



The isonitrils of *methyl*, *ethyl*, and *amyl* are formed in like manner. On mixing the corresponding sulphocarbimide with triethylphosphine, a rise of temperature takes place, and the odour disappears, owing to the formation of a compound analogous to the sulphocarbophosphamide above mentioned. When the mixture is further heated under pressure, magnificent crystals of triethylphosphine sulphide are deposited on cooling, and at the same time the pungent odour of the isonitril of the series is developed (Hofmann, *Zeitschr. f. Chem.* vii. 29).

**ISOPHTHALIC ACID.** See PHTHALIC ACID.

**ISOPURPURATES.** See PURPURATES.

**ISOPYRE.** Under this name are included various massive minerals found in European collections. The original specimens from St. Just in Cornwall, to which the name was given in 1827 by Haidinger, were analysed by Turner, who found in them 47.69 p.c.  $\text{SiO}_2$ , 13.91  $\text{Al}_2\text{O}_3$ , 20.07  $\text{Fe}^{\text{O}}\text{O}_3$ , 1.94 CuO and 15.43 CaO (Wi. 435). The colour of this mineral is jet-black, with a few red spots resembling those of blood-stone; lustre vitreous; streak pale grey; hardness 6.5; sp. gr. 2.912; fracture conchoidal; slightly magnetic. One specimen occurs on granite associated with tourmalin (Schorl). An analysis by Maskelyne & Flight (*Chem. Soc. J.* [2], xi. 1049) gave:

$\text{SiO}_2$		$\text{Al}_2\text{O}_3$	$\text{Fe}^{\text{O}}\text{O}_3$	FeO	CuO	MgO	K <sup>2</sup> O	Na <sup>2</sup> O	Li <sup>2</sup> O	CuO	F.	H <sup>2</sup> O
uncombined	combined											
14.33	31.82	12.59	3.03	15.91	13.21	1.66	1.15	0.70	trace	1.10	2.28	0.85 = 98.65.

The reaction of the mineral with potash showed that 15.19 p.c. of the silica was present as opal, and that it was mixed with a mineral approaching in composition to the felspar type.

Other minerals designated as isopyre consist mainly of silica.

a. From St. Just. Dark brown, compact, massive, and with conchoidal fracture and semi-vitreous lustre. It carries opal in botryoidal forms in cavities, and a dendritic accompaniment, probably of pyrolusite, or perhaps melanoconite, occurs occasionally as an infiltration. Native copper occurs with it very sparsely. Hardness = 7. Contains

$\text{SiO}_2$	$\text{Fe}^{\text{O}}\text{O}_3$	CuO	H <sup>2</sup> O
93.04	3.23	1.38	2.72 = 100.37.

Part of the iron appears, however, to be present as monoxide: the powdered mineral has a buff colour, changing on ignition to light brick-red.

B. From Suckasunny, New Jersey. Dark olive-green compact mass, with a conchoidal and rather splintery fracture, slightly translucent, and with a waxy lustre. A similar mineral from the same locality closely resembles the brown Cornish variety in colour and characters. The green variety, when finely powdered, is of a pale greenish grey colour, changing by ignition to buff. It contains:

$\text{SiO}_2$	$\text{Fe}^{\text{O}}\text{O}_3$	CuO	MgO	H <sup>2</sup> O
92.79	2.10	0.35	0.35	4.07 = 99.66.

No portion of the small amount of iron in this mineral appears to be present as monoxide.

A liver-brown mineral ( $\gamma$ ) associated with one ( $\delta$ ) having the appearance of jasper, and also coming from St. Just, closely resembles the mineral a. The jasper-like mineral associated with it presents in parts the dull aspect and other characters of massive ferruginous quartz; elsewhere its characters are those of a jasper opal. Iron ochre, pyrolusite, and melanoconite accompany it in the former specimens. It occurs in a siliceous matrix with some of the characters of a gossan, and is associated with quartz and a finely grained chlorite and ferric oxide.

These two minerals have the following composition:—

	$\gamma$	$\delta$
Silica . . . . .	73.15	76.22
Alumina . . . . .	0.06	0.15
Ferric oxide . . . . .	9.53	9.05
Ferrous oxide . . . . .	10.02	8.86
Lime . . . . .	0.30	0.32
Magnesia . . . . .	0.11	0.20
Water . . . . .	5.46	4.76
Copper oxide . . . . .	—	0.63
	99.23	100.19

After treatment with potash,  $\gamma$  left a residue amounting to 25 p.c., and  $\delta$  one of 25.63 p.c. It is evident that these minerals consist of opal in different degrees of impurity.

The presence of ferrous oxide in all these varieties of opal may explain the mineralogical similarity to which their association under the name of isopyro in our collections is due. Their source has probably been mineral waters charged at once with silica and a ferrous carbonate. That they are only the more characteristic specimens, occurring in large deposits of the same kind, is evidenced by the character of the lodes charged with copper ores at Botallack or the Bilston mines, where the neighbouring granites offer the conditions for furnishing the material (Maskelyne n. Flight).

**ISOPYRINE.** An alkaloid obtained by boiling the mashed roots of *Isopyrum thalictroides* with water, filtering, evaporating to a syrup, and precipitating with ammonia. The isopyrine may be dissolved out of the dried precipitate with ether. It has a bitter taste, and forms an amorphous hydrochloride.

**Pseudoisopyrine.**—When the residue obtained by boiling the roots with water is digested with alcohol, the resulting liquid evaporated till all alcohol is removed, ammonia added to the watery residue, and the ensuing precipitate treated with ether, another alkaloid is dissolved out, which crystallises in stellate groups of needles. The two alkaloids may, if present together in solution, be separated by adding very dilute hydrochloric acid and ammonium chloride, whereby pseudoisopyrine only is thrown down as chloride.

These alkaloids have not yet been further examined (F. A. Hartsen, *Chem. Centr.* 1872, 523).

**ISOTAURINE.** See TAURINE.

**ISURETINE**,  $\text{CH}^{\text{N}}_2\text{O} = \text{C} \begin{Bmatrix} \text{NH} \\ \text{NH.OH.} \\ \text{H} \end{Bmatrix}$  (Lossen a. Schifferdecker, *Zeitschr. für*

*Chem.* vii. 594; *Ann. Ch. Pharm.* clxvi. 295). A base isomeric with urea produced by digesting an alcoholic solution of hydroxylamine with strong hydrochloric acid at  $40^\circ$ – $50^\circ$ . On evaporating the liquid, isuretine is deposited in large crystals which may be purified by recrystallisation from aqueous alcohol.

Isuretine is very soluble in water, less soluble in alcohol, slightly in ether, insoluble in benzene. It has a strong alkaline reaction, and melts with incipient decomposition at  $104^\circ$ – $105^\circ$ . The crystals, which somewhat resemble those of urea, have been examined by Klein (*Ann. Ch. Pharm.* clxvi. 179). They have very smooth faces, which reflect moderately well, but after a few minutes' exposure to the air, become dull, from absorption of moisture, and the previously sharp edges begin to melt off. The angular measurements are therefore attended with considerable difficulty.

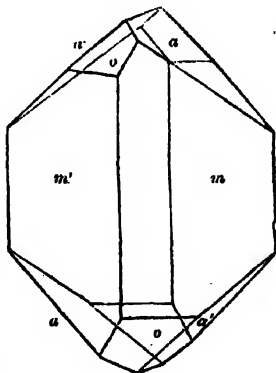
The crystals (fig. 18) belong to the rhombic system,  $a : b : c = 0.65563 : 1 : 1.12041$ . Fundamental angles:  $\infty P : \infty P = 113^\circ 30'$ ;  $P_\infty : P_\infty = 83^\circ 30'$ . Observed faces:  $\infty P$  ( $m$ ),  $P_\infty$  ( $a$ ),  $P_{\frac{1}{2}}$  ( $o$ ), more rarely  $0P$ , still more rarely  $r \frac{P}{2}$ . Character prismatic in the direction of  $\infty P$ . Colour white; only the small crystals are perfectly transparent. No distinct cleavage perceptible.

The plane of the optic axes is  $a b$ . The first positive median line is at right angles to the perpendicular truncation of the acute lateral edge, and therefore coincides with  $b$ . The optic axes are more divergent for the red than for the blue rays.

Very remarkable is the occurrence in this body of the rhombic sphenoid,  $1 \frac{P}{2}$ , which is much more frequently developed than its correlative,  $r \frac{P}{2}$ . Here, indeed, it is impossible to overlook a certain tendency to hemihedral formation, which is common to the two isomeric bodies, urea and isuretine; in the former the quadratic primary pyramid likewise occurs as a sphenoid.

Solutions of isuretine give with copper sulphate a dirty green, with lead nitrate a white

Fig. 18.

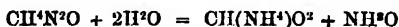


precipitate, with *mercuric chloride* a precipitate which is at first bulky and yellowish-white, afterwards denser and dark yellow. With *silver solutions* no precipitate is deposited, but on applying heat the silver is reduced. *Ferric chloride* gives a reddish-brown colour, which disappears on addition of hydrochloric acid.

*Isurettine hydrochloride*,  $N^2CH^2O.HCl$ , crystallises in deliquescent rhombic tables, excessively soluble in water, melting at about  $60^\circ$ . The *sulphate*,  $(N^2CH^2O)^2H^2SO_4$ , *acid oxalate*,  $N^2CH^2O.C^2O^2H^2$ , and *picrate*,  $N^2CH^2O.C^6H^3(NO^2)^3O$ , are all crystallisable.

*Decomposition by Heat*.—Isurettine heated beyond its melting point, readily decomposes, evolving a small quantity of permanent gas, and giving a considerable sublimate of ammonium carbonate. A yellowish amorphous residue is left, from which boiling water extracts a yellowish substance very slightly soluble in water, and presenting the composition and essential characters of ammeline,  $N^2C^2H^2O^2$ . The portion of the residue insoluble in boiling water has substantially the composition of ammeline. This residue boiled with nitric acid furnishes cyanuric acid.

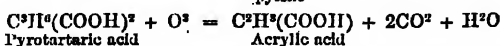
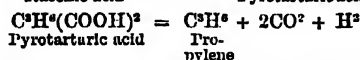
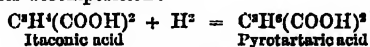
*Decomposition by Hot Water*.—A solution of isurettine in its own weight of water evaporated on a water-bath undergoes decomposition, with evolution of nitrogen, ammonia, and carbonic anhydride. The mother-liquors contain urea, ammonia, guanidine, and other substances apparently uncrystallisable. When dilute solutions are employed, very little urea is formed, the isurettine takes up the elements of water, and a solution of ammonium formate is produced; hydroxylamine,  $NH^2O$ , which is formed at the same time, being represented only by its products of decomposition, viz., nitrogen, ammonia and water:



A similar reaction takes place when isurettine is boiled with dilute sulphuric acid, formic acid distilling over, and the residual solution containing ammonia and hydroxylamine.

An aqueous solution of isurettine, shaken up with *benzoyl chloride*, deposits dibenzhydroxamic acid,  $NH(C^6H^5O)^2O$  (p. 155).

**ITACONIC ACID**,  $C^3H^2O^4$ . When a saturated solution of potassium itaconate is submitted to *electrolysis*, carbon dioxide is evolved from the positive electrode, together with a modification of allylene which does not precipitate ammoniacal silver nitrate. This allylene unites with bromine, forming a dibromide,  $C^3H^2Br^2$ , and this, when heated with excess of bromine, forms a crystalline tetrabromide,  $C^3H^2Br^4$ . During this reaction a small quantity of hydrobromic acid is formed, indicating probably that the allylene is accompanied by propylene. After the electrolysis has proceeded for some time, a modification of allylene capable of precipitating ammoniacal solution of silver nitrate is evolved. This may perhaps be due to the decomposition of mesaconic acid, which, together with acrylic acid, is found in the solution after the electrolysis. No pyrotartaric acid has hitherto been found among the products, but if we suppose it to be formed, the propylene, carbon dioxide, and acrylic acid may be regarded as products of its decomposition:—



Potassium *citraconate* gives by electrolysis carbon dioxide and an allylene containing an atom of hydrogen replaceable by metals, apparently also acrylic and mesaconic acids. Potassium *mesaconate* gives carbon dioxide and allylene, which is precipitated by a silver solution. The other products of the decomposition are probably acrylic and itaconic acids.

The formula of the three allylenes is not decided, but the one obtained from itaconic acid is not identical either with ordinary allylene or with those obtained from citraconic and mesaconic acids (G. Aarland, *J. pr. Chem.* [2], iv. 376; vi. 236; vii. 142).

Neutral itaconate of sodium or ammonium gives with *ferric chloride* a brown precipitate soluble in excess of the reagent. This solution when heated redeposits the precipitate, which, however, dissolves again as the solution cools (Aarland).

Itaconic acid in moderately strong solution heated for some hours with *neutral potassium sulphite*, yields the potassium salt of sulpho-pyrotartaric acid,  $C^3H^2SO_3$ , which is obtained as a syrupy liquid by evaporation, and as a gummy mass by precipitation with alcohol (Wieland, *Ann. Ch. Pharm.* clvii. 34).

When itaconic acid is heated with anhydrous *hydrocyanic acid* to a temperature of

140°-150°, a syrupy mass is obtained, which, after exposure to the air to allow the excess of hydrocyanic acid to escape, yields by fractionation citraconic acid. The syrupy mass probably contains a hydrocyanic addition-product,  $C^6H^7NO^4$ , although all attempts to isolate this compound failed; but if this syrupy mass is allowed to remain under the air-pump till it has lost the odour of hydrocyanic acid, a gentle warmth suffices to reproduce this odour, and treatment with soda causes the liberation of ammonia and the production of mesaconic acid (Barbaglia, *Deut. Chem. Ges. Ber.* vii. 465).

**ITAMALIC ACID**,  $C^6H^6O^4$ . *Chloritamalic acid*,  $C^6H^7ClO^4$ , is obtained by passing chlorine into a solution of sodium itaconate, adding hydrochloric acid, evaporating to dryness in a retort over the water-bath, and exhausting the residue with ether. The ethereal solution after some time deposits chloritamalic acid in the crystalline form.

Chloritamalic acid differs from chlorocitramalic acid in forming very much smaller crystals, and in not giving a crystalline precipitate with barium acetate, even when the solution is very concentrated. It forms salts with difficulty, chiefly because of its proneness to decomposition in presence of bases.

## J

**JADEITE.** See NEPHRITE.

**JEFFERSONITE.** This mineral, a variety of augite (iii. 443), occurs at Franklin, New Jersey, in laminae formed by the cleavage of monoclinic crystals in the direction of the orthopinacoid  $\infty P\infty$ . The cleavage is perfect in this direction, difficult in the direction of the clinopinacoid ( $\infty P\infty$ ). Angle  $\infty P\infty : (\infty P\infty) = 90^\circ 45'$ . The mineral is translucent in thin layers, with a vitreous lustre, and breaks with an unctuous but unequal fracture. Colour, deep green; hardness, 5.5; density, 3.63. Before the blowpipe it melts to a slightly magnetic black enamel, and gives with sodium carbonate and nitre a strong reaction of manganese. It is not attacked by acids.

Analysis gave—

SiO <sup>2</sup>	AlPO <sup>4</sup>	CaO	MnO	FeO	MgO	ZnO	H <sup>2</sup> O
45.95	0.85	21.55	10.20	8.91	3.61	10.15	0.35 = 101.57

The oxygen ratio calculated from these numbers leads to the formula  $RO.SiO^2$ . The percentage of zinc here given is much larger than that found in former analyses (Pisani, *Compt. rend.* lxxvi. 237).

**JERVIC ACID.** An acid occurring in white hellebore root (p. 641).

**JERVINE.** This alkaloid, first obtained by Simon from the root of *Veratrum album* (iii. 445), exists also in *V. viride*, from which may be prepared pure by the following process:—The finely powdered root is thoroughly exhausted with strong spirit, and the tincture is evaporated to a small bulk, acidulated with acetic acid, and mixed with water. The resin thereby precipitated is separated by filtration; the filtrate is concentrated, and rendered strongly alkaline with sodium carbonate; the resulting precipitate is dried, and boiled with strong spirit, till nothing more is dissolved; the alcoholic solution is evaporated to dryness; and the residue digested in hot, very dilute sulphuric acid. The granular powder, which separates on cooling, is jervine sulphate, which, after washing, is decomposed by boiling it with strong solution of sodium carbonate. Jervine then separates as a granular powder, which is washed, dissolved in acetic acid, and again precipitated by ammonia.

When a minute fragment of jervine is moistened on a glass slide, with a drop of strong sulphuric acid, it changes first to a straw-yellow, and then gradually to a green colour. This reaction is characteristic and delicate (C. Mitchell, *Pharm. J. Trans.* iv. 706).

**JUGLANDIC ACID.** An acid said to be obtained from the bark of *Juglans cinerea*, and described as crystallising in short orange-yellow needles, apparently related to chrysophanic acid (Thiebauld, *Pharm. J. Trans.* [3], ii. 1033).

**JULIANITE.** A mineral occurring in the Frederiko Juliane Mine, at Rudelstadt, in Silesia, in small botryoidal crystalline aggregations, penetrating calcite or covering druses of that mineral. Crystalline characters, indistinct; form, cube in combination with dodecahedron. Hardness very small. Brittle. Fracture, splintery or slightly conchoidal. Specific gravity, 6.12. Colour of fresh surface, dark lead-grey, with a

slight tinge of red, soon turning black. Composition: copper, 52.298; iron, 0.787; silver, 0.538; sulphur, 26.503; arsenic, 16.782; antimony, 1.421 = 98.329. The deficiency, 1.651 per cent., is believed to be due to loss of arsenic, and calculated as such in the formula,  $(\frac{1}{10}\text{As}, \frac{1}{10}\text{Sb})^2 (\text{Cu}; \text{Ag})^2 \text{S}^6$ .

Julianite is isomeric and isomorphous with bornite (H. Websky, *Jahrbuch f. Mineralogie*, 1872, 218).

**JUNIPER.** E. Donath (*Dingl. pol. J.* cccviii. 300) has analysed the berries of *Juniperus communis* with the following result:

Water . . . . .	29.44	Juniperin . . . . .	0.37
Essential oil . . . . .	0.91	Pectin . . . . .	0.73
Formic acid . . . . .	1.86	Protein substances . . . . .	4.45
Acetic acid . . . . .	0.94	Sugar . . . . .	29.65
Malic acid . . . . .	0.21	Cellulose . . . . .	15.83
Fat, resembling wax . . . . .	0.64	Mineral constituents . . . . .	2.33
Green resin . . . . .	8.46		
Hard brown resin . . . . .	1.29		97.11

## K

**KAINITE**,  $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ . This double salt, originally found at Stassfurt (1st Suppl. 764), occurs also at Kalusz in Galicia, in two horizontal beds from 70 to 80 feet thick, without any intervening layer, and mixed with only small quantities of sylvin and rock-salt.

The first three of the following analyses are by K. v. Hauser (*Jahrb. geol. Reichsanstalt*, xx. 141). A, gives the composition of the principal deposit consisting of granular black-brown masses with small yellowish and white spots; B, light yellow laminar particles often occurring in great numbers; C, honey-yellow transparent imbedded particles occurring but rarely. D, is an analysis of the same by Tschermak (*Wien. Acad. Ber.* (1 Abth.) lxiii. 311). E, is the composition of the pure salt calculated according to the formula above given.

	A	B	C	D	E
$\text{SO}_4$	20.46	20.26	32.24	32.34	32.19
Cl	28.01	30.84	15.03	14.56	14.28
MgO	10.16	10.17	16.12	16.75	16.10
K	16.38	13.07	15.25	15.66	15.69
Na	7.97	11.60	0.69	0.03	—
Water	14.36	14.12	21.37	20.73	21.74
Clay	3.41	0.16	—	—	—
	100.76	100.22	100.70	100.07	100

One part of water at  $17^\circ$  dissolves 0.467 part of the anhydrous crude kainite; the density of the saturated solution is 1.256 (v. Hauser).

According to A. Jacot (*Compt. rend.* lxxiii. 995) the beds of Kalusz yield daily more than 1,000 Austrian centners (81,100 kilos.) of potassium chloride.

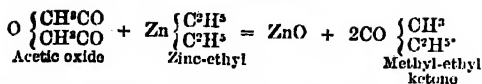
**KALUSZITE.** See SYNGENITE.

**KARAKA.** The nut of the New Zealand karaka tree (*Corynocarpus levigata*), though poisonous in its natural state, is one of the staple articles of vegetable food used by the natives. The nuts are partially baked in earth ovens, then washed for some time in a stream of water, which removes the poisonous matter, and finally dried and stored for use.

The bitter substance, karakin, removed by the water crystallises in beautiful radiate needles. It exhibits the characters of a glucoside rather than those of an alkaloid (W. Skey, *Chem. News*, xxvii. 190).

**KELP.** On the estimation of iodine in kelp liquors, see IODINE (p. 672).

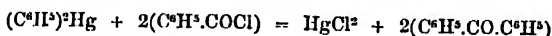
**KETONES.** *Formation.*—As ketones are formed by the action of the zinc-compounds of the alcohol-radicles on the chlorides of acid-radicles (1st Suppl. 766), it might be expected that they would also be formed by the action of the same zinc-compounds on the oxides or anhydrides of the same acid-radicles, e.g.:



Sjostoff, however, finds (*Zeitschr. f. Chem.* [2], vi. 104) that the action of ready-formed zinc-ethyl on acetic oxide does not yield any definite product; but by bringing the acetic oxide in contact with zinc-ethyl in the nascent state, which may be effected by treating a mixture of ethyl-iodide and acetic oxide [ $2\text{C}^2\text{H}^5\text{I} + (\text{C}^2\text{H}^5\text{O})^2\text{O}$ ] in a cooled vessel with pulverised zinc-sodium, the desired result may be obtained. The reaction is complete in 20–30 hours, and on carefully mixing the contents of the flask with water, distilling and treating the distillate with potash, an oil separates, part of which distils below  $100^\circ$ , and forms a crystalline compound with sodium bisulphite. The ketone separated from this compound by potash boils at  $77\text{--}80^\circ$ , and has the composition of methyl-ethyl ketone,  $\text{C}^4\text{H}^8\text{O}$ .

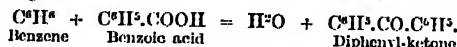
The same process, with the substitution of methyl-iodide for ethyl-iodide, yields common acetone,  $\text{CO}(\text{CH}^3)^2$ .

Ketones containing phenyl may be formed:  $\alpha$ . By the action of mercury-diphenyl on chlorides of acid-radicles; e.g. diphenyl-ketone from mercury-diphenyl and benzoyl-chloride:



(R. Otto, *J. pr. Chem.* [2], i. 144).

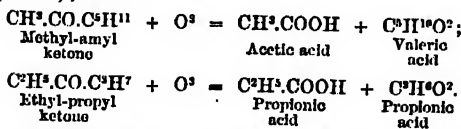
$\beta$ . By heating a mixture of an aromatic hydrocarbon and benzoic acid with phosphorus pentoxide, e.g.:



In like manner *tolyl-phenyl ketone*,  $\text{C}^7\text{H}^7.\text{CO.C}^6\text{H}^5$ , may be prepared from toluene, and *naphthyl-phenyl ketone*,  $\text{C}^{10}\text{H}^7.\text{CO.C}^6\text{H}^5$ , from naphthalene (Kollarits a. Merz, *Deut. Chem. Ges. Ber.* vi. 536).

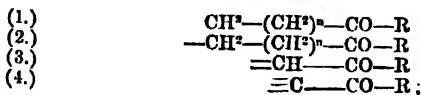
Respecting E. Schmidt's method of preparing ketones by heating the calcium salt of the corresponding acid mixed with calcium carbonate in an iron tube, see BUTYRONNE (p. 228).

*Oxidation of Ketones.*—When a ketone containing only normal alcohol-radicles is treated with a mixture of potassium dichromate and dilute sulphuric acid, two fatty acids are produced, the action taking place in such a manner that the higher of the two alcohol-radicles is oxidised, while the other remains united with the carbonyl (Popoff, 1st *Suppl.* 765); thus:



From subsequent experiments, and a comparison of the results obtained by Kolbe, Wurtz, Erlenmeyer, Butlerow, and Wanklyn, Popoff (*Ann. Ch. Pharm.* clxi. 285; *Deut. Chem. Ges. Ber.* v. 381) deduces the following more general conclusion:—

In the oxidation of ketones in which one of the alcohol-radicles united with the carbonyl (R in the following general formulæ) is phenyl or methyl, or in some cases thyl, viz.:



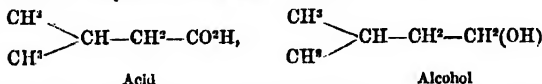
the carbonyl always remains united with the radicle R, while the other radicle is oxidised. If this other radicle belongs to a normal alcohol (1), it is oxidised to a normal acid; if it is an iso-alcohol-radicle (2), it yields an iso-acid; a secondary alcohol-radicle (3) in like manner yields a ketone; and a tertiary radicle (4) is split up.

Now when a ketone is formed by distilling a mixture of the calcium salts of two fatty acids, or of a fatty and an aromatic acid, or by the action of the zinc-compound of an alcohol-radicle on an acid chloride, the acid-radicle yields the carbonyl required to form the ketone; and when this ketone is subjected to oxidation, the carbonyl remains united with the alcohol-radicle R, while the other alcohol-radicle derived from the acid is oxidised according to the laws of the oxidation of ketones; or, in other words, alcohol-radicles. Hence the preparation and oxidation of a properly chosen ketone

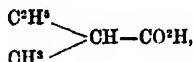
furnishes the means of first separating the oxidised carbon from an acid, and then oxidising the alcohol-radicle united with this carbonyl in such a manner that the constitution of the acid, and therefore, also, of the corresponding alcohol, may be inferred from the products of oxidation of the ketone.

As an example of this method of determining the constitution of acids and alcohols, Popoff describes the reactions of the phenyl-ketone from the valeric acid obtained from fermentation amyl-alcohol. The amyl-alcohol boiled at 130–131.5° and had a rotatory power = -2.4°; the valeric acid obtained from it boiled at 174–176° and had a rotatory power = +4.4°. It consisted, therefore, in great part of the optically inactive acid. On distilling a mixture of the calcium salt of this acid with an equivalent quantity of calcium benzoate, and rectifying the distillate, a liquid was obtained boiling at 225–226°, and having the composition of butyl-phenyl ketone, C<sup>6</sup>H<sup>5</sup>.CO. C<sup>4</sup>H<sup>9</sup>. This liquid yielded, by oxidation, benzoic and iso-butyric acids, the latter being recognised by the characters of its calcium and silver salts. A small quantity of acetic acid was likewise produced.

The formation of benzoic acid shows that the carbonyl and phenyl groups remain united in the butyl-phenyl ketone. The production of iso-butyric acid proves that iso-butyl was present in the ketone, and, therefore, in the valeric acid and in the amyl-alcohol. Since the valeric acid employed consisted mainly of the inactive modification, and since iso-butyric acid was produced in quantity, it follows that the inactive valeric acid and the inactive amyl-alcohol contain iso-butyl:



This result confirms the conclusions of Erlennmeyer, Frankland and Duppa, and Butlerow, respecting the constitution of fermentation amyl-alcohol. The acetic acid was perhaps due to impurity in the product, or to a secondary and irregular oxidation of the ketone, or to the presence of a small quantity of active valeric acid. This possibility may be ethyl-methyl-acetic acid:



the ketone of which would certainly yield acetic acid.

On the compounds of ketones with Mercuric Oxide, see ACETONE (p. 13).

**KIDNEY-BEAN.** See BEAN (p. 126).

**KIESERITE.** A mineral found by A. Simony in the rock-salt of Hallstatt has been recognised by Tschermak (*Jahrbuch f. Mineralogie*, 1871, 758) as kieserite. It is found in coarse-grained yellowish masses, the cavities of which are lined with monoclinic crystals whose axes  $a : b : c = 0.91474 : 1 : 1.7445$ ; angle  $ac = 88^\circ 53'$ . The habit of the crystals resembles that of lazulite, and is determined by the faces -P and +P, with  $+\frac{1}{2}P$ , -P $\infty$ , and (P $\infty$ ) subordinate. Hardness greater than 3: Analysis  $a$  is by Tschermak;  $b$  by H. Wieser (*ibid.* 642);  $c$  gives the values calculated according to the formula  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ :

	SO <sup>3</sup>	MgO	FeO	Fe <sup>2</sup> O <sup>3</sup>	Na <sup>2</sup> O	Cl	H <sup>2</sup> O
$a$	57.92	29.09	—	0.25	—	—	13.40 = 100.66
$b$	57.87	28.89	0.05	—	0.05	0.06	13.24 = 100.16
$c$	57.97	28.99	—	—	—	—	13.04 = 100

Sp. gr. of  $a = 2.569$ ; of  $b = 2.5645$ .

Kieserite forms about 12 p.c. of the refuse salt (*Abraunsalz*) of Stassfurt, and is separated therefrom by its sparing solubility in cold water. This refuse salt having been boiled down to extract the potassium salts, the residue is placed in a funnel-shaped vessel and washed with cold water; this separates the soluble salts from the mixture of other partially soluble compounds, kieserite, anhydrite, clay, sludge, &c., which may be separated to a great extent by their difference of specific gravity. The kieserite is then placed in iron frames and crystallised by heat. In this process a part of the compound is converted into the salt containing 7 mol. of water, and the mass is sent into commerce as block kieserite containing 60 p.c.  $\text{MgSO}_4$ . One of the principal uses of this kieserite seems to be for the washing of wool; it is also used for the preparation of 'permanent white' by precipitation with barium chloride, and for the manufacture of crystallised glauber salts, with the sodium chloride which is a by-product of the refuse salt. 2 molecules of kieserite and 1 of calcium hydrate heated with water solidify to a gelatinous mass containing  $\text{CaSO}_4 + \text{MgSO}_4 + \text{MgO}$ . This, on being strongly heated, powdered, and mixed with water, quickly hardens to a



marble-like mass, which may be polished and to a certain degree withstands damp (H. Grüneberg, *Deut. Chem. Ges. Ber.* v. 840).

**KILLAS** (J. A. Phillips, *Phil. Mag.* [4], xli. 87).—This is the name applied by Cornish miners to all sedimentary cleavable rocks. The geological age of these rocks has not been determined beyond that they belong to the palæozoic era, and it is believed that they are of Devonian age. They enclose five large and several smaller 'islands' of granite, and are, as well as the granite itself, traversed by dykes of granitic and porphyritic rock called *elvans*, by trap dykes, by copper and tin lodes, and by various cross courses, including *fucans*, or fissures filled with clay. Typical killas is a grey, bluish-grey, or greenish-grey clay-slate, and, when weathered, is brownish-yellow or buff. It is usually exceedingly fissile with the planes much contorted, but is often more compact near its junction with the granite. The sections examined in the microscope by 'a low power' were magnified 60, or by a 'high power' about 400 linear.

I. *Killas from Polgooth Mine, adit level*; sp. gr. = 2.60.—This is a very soft slate of a light-grey colour, marked in places with a darker shade or yellow tinge. By transmitted light under a low power, thin sections exhibit no structure, but appear as a milky-white mass, enclosing moss-like semi-crystalline markings of a brownish-green, and traversed by fissures filled with crystalline transparent quartz. With a high power it is found to be composed of an aggregate of minute granules intimately blended together without definite outlines, and to enclose some grains of oxide of iron and apparently fragments of hornblende, and some patches of a chloritic mineral.

II. *Killas from Polgooth Mine, 80 fathoms level*; sp. gr. = 2.74.—This specimen, much harder than the above, is of a grey colour, strongly marked with reddish-brown. Here the microscope detected no difference excepting that the grains of oxide of iron were larger but less numerous, and that there were fewer of what appeared to be broken crystals of a hornblende mineral. The granular fragments are larger and more distinct, their larger surfaces being nearly parallel with the planes of cleavage of the slate. The chloritic mineral is again very abundant, and peculiar markings are observed about its margin.

III. *Killas from Polgooth Mine, 100 fathoms level*; sp. gr. = 2.73.—At this depth the killas is much harder than that found at shallower levels, is of a greenish-grey, slightly streaked and spotted with yellow. The sections resemble those from the 80 fathoms level, but contain no hornblende and fewer chloritic patches.

IV. *Killas from Polmar Mine, 40 fathoms below the surface*; sp. gr. = 2.68.—This clay-slate is much contorted, dividing readily in curved laminae, with glossy surfaces bearing wavy lines resembling minute ripple-marks. It is of a medium grey, and slightly yellow in places. Its sections resemble those of the Polgooth specimens. Granules of quartz are disseminated through the finely-grained matrix, which derives its greyish tint from chlorite, and is minutely divided by a system of markings made up of pairs of parallel lines, each about  $\frac{1}{1000}$ th of an inch long, and  $\frac{1}{5000}$ th of an inch apart.

V. *Slate from 'Sanctuaries' near St. Austell*; sp. gr. = 2.52.—This is light grey and buff in colour, and appears to be weathered. It divides with difficulty into laminae, the surfaces being without polish. It is divided by headings variously coloured, apparently by infiltration of water containing oxide of iron.

VI. *Killas from Dolcoath Mine, 215 fathoms level*; sp. gr. = 2.71.—This rock is exceedingly hard, the cleavage imperfect, and its prevailing colour dark grey. Freshly fractured surfaces exhibit numerous minute, brilliant, indistinct crystals, probably of some hornblende mineral. With a low power its sections appear to be made up of some transparent angular particles, giving colours with polarised light; the greenish patches disseminated through the mass are probably chlorite. With a high power are seen black grains of magnetite and titaniferous iron, and fan-like aggregations of transparent acicular crystals, often diverging from a particle of oxide of iron. Similar crystals also cross each other in all directions, and are probably hornblende or schorl. Mechanically imbedded are rounded fragments of mica, and of a semi-translucent mineral not sufficiently opaque for oxide of iron.

VII. *Killas from Botallack, Penzance, surface near lode*; sp. gr. = 2.95.—This is a very hard, dark greenish-grey rock, containing minute crystals of pyrites; its cleavage being to a great extent obliterated by metamorphism, it breaks into roughly tabular masses whose planes approximate to those of original cleavage. The low power shows an amorphous base, often green, due probably to chlorite, and enclosing transparent crystals and crystalline patches, often fringed with acicular crystals, which give brilliant colours with polarised light. With a high power long slender crystals, probably of apatite, and minute triclinic crystals, possibly of axinite, are seen.

VIII. *Rock from Botallack, 130 fathoms*; sp. gr. = 2.82.—A very dark green specimen, with traces of lighter shade and no cleavage; is slightly magnetic, and encloses in places minute crystals of pyrites. The grains of oxide of iron are more numerous than in specimens obtained nearer the surface. It contains fewer long crystals than the surface rock, and is traversed by minute veins of quartz enclosing transparent acicular crystals, probably of hornblende. From its physical constitution and the large amount of magnesia it contains, it may be regarded as an impure serpentine.

IX. '*Best roofing slate, Delahole*'; sp. gr. = 2.81.—Under a low power this slate shows no distinct structure, but is thickly dotted with dark spots; but with a high power numerous clusters, about  $\frac{3}{1000}$ th of an inch in diameter, of reddish-brown crystals appear. These result from the aggregation of several hexagonal plates of a substance which, according to Mr. Sorby's examination, consists of more or less altered specular iron. The matrix is, moreover, traversed in all directions, but especially in planes parallel to the cleavage, by long transparent crystals which are brilliantly coloured by polarised light. Both brown and white crystals have been formed *in situ*.

X. *Diorite, 'Sanctuaries,' St. Mewan*; sp. gr. = 2.97.—This rock is of a dark green colour verging on black, is exceedingly hard and tough, distinctly crystalline and magnetic. Thin sections exhibit unmistakable evidence of extensive alteration. The felspar does not generally present any distinctive characteristics, although in a few instances the parallel striping peculiar to triclinic varieties was observed. The rock also contains semi-transparent yellowish-brown crystals, probably hornblende, a green mineral of fibrous structure which is believed to be a variety of hornblende, many black grains of oxide of iron, some well-defined hexagonal crystals, probably apatite, and an abundance of a green chloritic mineral. This diorite has probably undergone much alteration.

XI. '*Greenstone, Blowing-House Hill, St. Austell*'; sp. gr. = 2.89.—This stone is very similar to the 'Sanctuaries' rock, but is of a somewhat duller aspect, and is divided by a series of oblique cross-headings, which impart to it a tendency to divide into rhomboidal masses; it is also less decidedly crystalline, and exhibits a grain resembling that of some varieties of metamorphosed schist. The sections show a compact felspathic matrix enclosing a few indistinct crystals of felspar, together with large quantities of the greenish chloritic mineral observed in the St. Mewan diorite, from which the greenstone differs but little in composition. The greenish mineral is arranged in approximately parallel bands and patches, many of the latter appearing to be partially decomposed hornblende crystals, and, though retaining at their centre to a certain extent their original structure and colour, have at the edges been transformed into chlorite or an allied mineral. The rock also contains many black grains of oxide of iron, and some hexagonal crystals, probably of apatite. It is believed to be an altered clay-slate.

XII. *Serpentinous rock, Menheniot*; sp. gr. = 2.77.—This is a moderately hard stone of a dark green colour, has a somewhat crystalline fracture and schistose structure, and is slightly magnetic. It occurs more or less intermixed with clay-slate, and beds of unaltered slate are found interstratified with it. It exhibits numerous resinous headings, many of which are coated with asbestos, with fissures containing calcite. Reniform concretions of saponite are frequently found in a clay apparently resulting from the decomposition of the principal rock. The microscope shows a highly metamorphosed rock consisting of an amorphous matrix, porphyritically enclosing yellowish-brown or green patches with indistinct crystalline forms, evidently pseudomorphs, with many grains of magnetite and crystals of what is probably schiller-spar or diallage.

XIII. *Serpentine, Lizard*; sp. gr. = 2.59.—The specimen is of a very dark green colour, in places verging on black and thickly spotted with red; it has a coarsely granular structure, is without any indication of foliation, and encloses imperfectly developed crystals.

XIV. *Orthoclase, 'Glass Mine,' Roche*; sp. gr. = 2.55.—This yellowish-white felspar occurs in granite containing considerable quantities of schorl, and is traversed by veins of milky quartz enclosing tourmaline and cassiterite. Professor Miller, of Cambridge, examined it crystallographically, and pronounced it to be a monoclinic felspar.

The following table exhibits the mean results of the analyses of these rocks:

	H <sup>2</sup> O	SiO <sup>2</sup>	TiO <sup>2</sup>	P <sup>2</sup> O <sup>5</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	Mn <sup>2</sup> O <sup>3</sup>	CaO	MgO	K <sup>2</sup> O	Na <sup>2</sup> O
I. . .	4.08	60.42	—	0.21	20.835	8.17	1.89	0.41	1.71	trace	0.77	1.55
II. . .	3.63	63.10	trace	—	20.15	3.51	2.955	trace	1.27	trace	0.95	3.14
III. . .	3.265	50.915	trace	—	20.785	13.415	4.92	—	1.62	—	0.93	4.08
IV. . .	6.58	49.265	trace	—	18.00	12.68	8.55	Fe <sup>2</sup> S <sup>3</sup> 0.82	2.13	trace	0.565	0.745
V. . .	6.16	53.30	trace	—	21.725	6.015	4.28	—	trace	0.75	2.92	4.195
VI. . .	1.16	67.315	0.13	—	20.845	2.885	1.66	—	2.025	trace	0.595	3.37
VII. . .	3.125	40.21	0.15	0.66	24.01	4.21	11.27	—	4.105	6.52	1.67	3.53
VIII. . .	11.09	32.98	trace	—	16.73	7.025	13.71	—	4.90	11.52	0.73	0.625
IX. . .	4.61	58.30	0.23	trace	21.89	7.055	2.57	—	0.395	1.095	2.45	1.135
X. . .	0.80	47.56	trace	0.11	17.16	13.06	9.30	Mn <sup>2</sup> O <sup>4</sup> trace	4.11	trace	2.30	5.45
XI. . .	1.00	47.505	trace	trace	17.00	11.75	10.71	0.41	6.285	trace	2.89	2.545
XII. . .	10.56	38.70	trace	trace	17.59	15.04	4.56	Cr <sup>2</sup> O <sup>3</sup> 0.14	4.98	6.00	trace	0.845
XIII. . .	15.52	38.72	—	—	2.995	1.905	5.07 and 0.29NiO	0.08	trace	34.565	0.325	0.765
XIV. . .	0.665	63.165	—	—	19.08	0.50	—	—	1.625	trace	10.37	2.40

X, likewise contains traces of sulphur; XII. and XIII. traces of an oxide of manganese.

**KINO.** On the occurrence of pyrocatechin in this substance, see PYROCATECHIN.

**KJERULFIN.** A mineral from Bamlo in Norway. It occurs massive with imperfect cleavage in two directions nearly at right angles to each other. Fracture, uneven and splintory. Lustre, fatty. Colour, pale red; translucent in thin fragments. Specific gravity = 3.15. Hardness = 4-5. When warmed it exhibits a faint white phosphorescence, and melts with some intumescence to a blistered enamel. Easily soluble in hot concentrated hydrochloric acid; somewhat less easily in nitric acid. With sulphuric acid it evolves hydrofluoric acid, and forms calcium sulphate. Analysis gave:

P <sup>2</sup> O <sup>5</sup>	MgO	CaO	Na <sup>2</sup> O	Fl	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>
42.22	37.00	7.56	1.56	4.78	1.50	5.40 = 100.02

with traces of potassium, iron, and sulphuric acid.

When the non-essential constituents are deducted, this composition corresponds with the formula  $2\text{Mg}(\text{PO})^2 + \text{CaF}_2$ , a small portion of the calcium being replaced by sodium.

Kjerulfin differs from wagnerite, which it resembles in many respects, by containing less fluorine and sodium, and more calcium, so that its solution in hydrochloric acid gives a precipitate with sulphuric acid, which is not the case with wagnerite (F. v. Kobell, *J. pr. Chem.* [2] vii. 272).

**KNOBELITE.** This mineral (iii. 447), hitherto known only as occurring at Ilmenau and Dannemora in Sweden, is found, according to Igelström (*Chem. Centr.* 1870, 198), in large quantities, in veins 4 metres thick, in the iron mine of Hillärg, Gudovilla parish, Dalarne Government, Sweden, embedded in heliofinta, together with magnetic iron ore, limestone, and a small quantity of magnetic pyrites. Analysis gave:

SiO <sup>2</sup>	FeO	MnO	CaO
33.14	40.96	19.35	6.35 = 100,

differing not inconsiderably from the former analysis of knobelite by Döbereiner 32.5 SiO<sup>2</sup>, 32.0 FeO, 35 MnO, iii. 447); nevertheless Igelström regards the mineral as knobelite on account of its similarity thereto in physical characters, and its property of gelatinising with hydrochloric acid. The larger proportion of ferrous oxide he attributes to intimately mixed magnetic oxide.

**KÖTTIGITE.** See PHOSPHATES.

**KOUMISS.** Observations on this beverage have been published by V. Jagielski *Pharm. J. Trans.* [3], i. 861, 885), who had the opportunity of studying its use and its action on the human body in the Stoppes of Russia. He points out that koumiss, when kept for some time in bottles, undergoes essential alteration, its amount of alcohol and carbonic acid continually increasing at the expense of the solid constituents of the mare's milk, and that this alteration is attended with the formation of acids,

especially lactic, acetic, butyric, and succinic. Koumiss in its different stages of fermentation, and therefore koumiss of various ages, is required in the treatment of different disorders. Koumiss may also be prepared from cow's milk, but on account of the much greater proportion of casein contained in the latter, the koumiss obtained from it is very different from that prepared from mare's milk. The spirit prepared from koumiss by distillation is called 'araca.'

Koumiss manufactured in Davos, Switzerland, in imitation of the true Russian koumiss, has a mean density of 1.1286 at 50°, and contains:

	In 100 grams	Per litre
Water . . . . .	90.346	1019.64 grams
Alcohol . . . . .	3.210	36.23 "
Lactic acid . . . . .	0.190	2.14 "
Sugar . . . . .	2.105	23.75 "
Albuminates . . . . .	1.860	20.90 "
Butter . . . . .	1.780	20.00 "
Inorganic salts . . . . .	0.509	5.74 "
Free carbonic acid . . . . .	0.177	2.00 "

This koumiss contains more sugar and less lactic acid than old Russian koumiss, and is probably prepared by adding a few per cent. of sugar to skim-milk, alcoholic fermentation being induced by the addition of yeast (H. Suter-Nacfi, *Deut. Chem. Ges. Ber.* v. 286).

#### KRANTZITE. See RESINS, FOSSIL.

**KYNURENIC ACID**, and **KYNURINE**. Kynurenic acid, discovered in dog's urine by Liebig (iii. 450), has been further examined by Schmidberg a. Schultzen (*Chem. Soc. J.* [2], x. 1028) who assign to it the formula  $C^9H^{11}N^2O^4$ , the free acid containing  $2H^2O$  of crystallisation, and the barium salt being  $C^9H^{11}BaN^2O^4 + 3H^2O$ . It is obtained from dog's urine by evaporation and addition of hydrochloric or nitric acid; it is practically insoluble in water, either hot or cold, or impregnated with hydrochloric or nitric acid, but slightly soluble in alcohol or ether. With baryta-water in excess it yields a soluble basic salt, which furnishes a precipitate of mixed carbonate and neutral salt on passing carbon dioxide through the solution, an appearance which misled Liebig to the idea that the free acid was thrown down from the barium salt by carbonic acid.

When heated to 265°, kynurenic acid evolves pure carbon dioxide and melts to a brown liquid. The product is mostly soluble in water, and on evaporation yields crystals having the composition  $C^{10}H^{11}N^2O^2$ . This substance, kynurine, is anhydrous, melts at 201°, and gives a crystalline hydrochloride,  $C^{10}H^{11}N^2O^2.2HCl + 4H^2O$ , and a crystalline platinum salt,  $C^{10}H^{11}N^2O^2.2HCl.PtCl^4$ ; it also gives a crystalline gold salt.

## L

**LABRADORITE.** See FELSPAR (p. 372). On the Labradorite rocks of Water-ville, New Hampshire, see E. S. Dana (*Sill. Am. J.* [3], ii. 48; *Chem. Soc. J.* [2], x. 227).

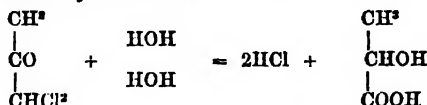
**LACTIC ACIDS**,  $C^3H^4O^3$ . 1. *Ethylidene-lactic acid*,  $CH^3-CHOH-COOH$ . *Formation from Sugar.*—a. *By Fermentation.*—The following mixture is recommended by C. O. Harz (*Vierteljahrsschrift pr. Pharm.* xx. 501; *Jahresb. f. Chem.* 1870, p. 561): 3 pts. milk-sugar, 36 pts. ordinary water, 0.5 to 0.75 pt. flour containing a large proportion of gluten, 1 or 2 tablespoonfuls of beer-yeast, 6 pts. of soda-crystals, or 3 pts. of sodium bicarbonate. When the fermentation has once been set up by milk-sugar, it may be continued by addition of cane-sugar.

b. *Without Fermentation.*—When 500 grams of grape-sugar are introduced into a capacious retort, together with  $1\frac{1}{2}$  pt. soda-ley of sp. gr. 1.34, and an equal volume of water, and heated in a water-bath, a very strong reaction takes place at about 96°, so that it is advisable not to operate with larger quantities at once. The temperature rises above 116°, and the liquid boils strongly without evolution of gas, acquiring a not unpleasant odour. On mixing it, after cooling, with a quantity of dilute sulphuric acid exactly sufficient to neutralise the soda, concentrating by evaporation, and

agitating with ether, lactic acid is dissolved out, together with pyrocatechin and greasy products. The lactic acid is abstracted from the ether by agitation with water and barium carbonate; the resulting barium salt is converted into zinc salt; and the latter is purified by crystallisation. The acid obtained from this zinc salt possesses all the characters of ordinary lactic acid. Its concentrated aqueous solution does not exhibit circular polarisation. As no volatile fatty acids are formed at the same time except formic acid, the lactic acid obtained by this process is much easier to purify than that which is prepared by fermentation, but the yield does not exceed 10 to 20 p.c. of the sugar employed. Cane-sugar or milk-sugar may be used in the process instead of grape-sugar (Hoppe-Seyler, *Deut. Chem. Ges. Ber.* iv. 346).

As neither lactic acid nor calcium lactate is altered by heating to 200° for several hours with water, attempts were made to produce lactic acid by the action of water on sugar or on paper at 200°, but always with a negative result. If a sufficient quantity of magnesia is added the sugar does not blacken, but still no lactic acid is formed (Hoppe-Seyler).

**Formation from Acetone.**—When dichloroacetone is heated to 200° for six hours with 20 times its volume of water, and the contents of the tube are successively treated with excess of silver oxide, hydrogen sulphide, and zinc-white, a zinc salt is obtained agreeing with that of ordinary lactic acid.



The exchange of Cl for HO is in this case accompanied by a transposition of the atoms within the molecule (Linnemann a. von Zotta, *Ann. Ch. Pharm.* clix. 247).

**2. Hydracrylic acid.**—This acid, which Beilstein obtained by the action of silver oxide and water on  $\beta$ -iodopropionic acid, and to which he assigned the formula ( $\text{H}^2\text{O}^1$ ), was shown by Moldenhauer to yield, by simple neutralisation with soda, a salt of lactic acid (*1st Suppl.* 770): hence it would appear to be only a modification of lactic acid; and this view is confirmed by the experiments of Wislicenus (*Deut. Chem. Ges. Ber.* iv. 532; *Ann. Ch. Pharm.* clxvi. 6).

To prepare hydracrylic acid, an aqueous solution of  $\beta$ -iodopropionic acid is boiled with silver oxide, the filtrate is treated with hydrogen sulphide, and after the excess of the latter has been expolled, the liquid is neutralised with sodium carbonate and evaporated. The residue is then digested with boiling alcohol of 75 p.c. which dissolves sodium hydracrylate, leaving undissolved the salts of three other acids which will be noticed further on (p. 721). The sodium salt may be purified by two or three recrystallisations from alcohol, and the pure acid obtained by decomposing it with sulphuric acid, agitating with ether, and leaving the ethereal solution to evaporate (Wislicenus). Or equal parts of the impure acid may be neutralised with lime and zinc oxide, the two solutions mixed, whereby a crystalline precipitate is formed consisting of zinc-calcium hydracrylate; and from this salt, purified by thorough washing or by recrystallisation, the pure acid may be obtained by removing the zinc with hydrogen sulphide, and the calcium by exact precipitation with oxalic acid (Heintz, *Ann. Ch. Pharm.* clvii. 291).

Hydracrylic acid remains, on evaporation of its ethereal solution, as a strongly acid syrup exactly like ordinary lactic acid. It is distinguished, however, from this and all the other modifications of lactic acid by the fact that, when heated, it does not yield a trace of lactide, but is resolved, almost without residue, into water and acrylic acid:  $\text{H}^2\text{O}^1 = \text{H}^2\text{O} + \text{C}^2\text{H}^2\text{O}^2$ .

Heated with iodine and potash-solution (Lieben's reaction) it does not yield iodoform. By oxidation with *chromic* or *nitric acid* it yields nothing but carbon dioxide and oxalic acid; with *silver oxide* it forms carbon dioxide, together with carbacetoxylic acid if the proportion of silver oxide is small, oxalic and glycollic acids if it is larger. With *melting potash*, the products are chiefly acetic and formic acids, together with a little oxalic acid and apparently also glycollic acid.

**Sodium hydracrylate**,  $\text{C}^2\text{H}^2\text{NaO}^2$ , crystallises in flat prisms with acuminate faces; deliquesces in moist air; is but slightly soluble in absolute alcohol, even at the boiling heat; somewhat more soluble in alcohol of 25 p.c., from which it crystallises in the anhydrous state on cooling; very soluble in dilute alcohol. It melts at 142°–143° without loss of weight to a colourless liquid, and solidifies to a crystalline mass on cooling. It gives off 1 mol. water slowly between 180° and 200°, more quickly at 50°, leaving a residue which has the composition of sodium acrylate,  $\text{C}^2\text{H}^2\text{NaO}^2$ , but differs from that salt in becoming heated in contact with water, and taking up again 10 water which it had lost.

*Silver hydracrylate*,  $C^6H^3AgO^3$ , forms delicate prisms and needles easily soluble in cold water, insoluble in alcohol.

*Calcium hydracrylate*,  $C^6H^{10}CaO^3 \cdot 2H^2O$ , loses water even when its solution is evaporated to a thin syrup, but on adding a little water to the residue, well-defined crystals are soon formed.

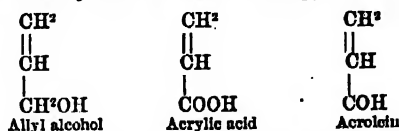
*Zinc hydracrylate*,  $C^6H^{10}ZnO^3 \cdot 4H^2O$ , also remains as a syrup when its solution is evaporated over the water-bath, but soon becomes crystalline on exposure to moist air. By spontaneous evaporation of the aqueous solution it is obtained in brilliant triclinic crystals. 100 pts. of the salt dissolve in 8 pts. water at  $16.5^\circ$  (Wislicenus).

*Zinc calcium hydracrylate*,  $C^6H^{10}ZnO^3 \cdot C^6H^{10}CaO^3$ , is obtained as a crystalline precipitate on mixing the concentrated solutions of its component salts, and in distinct crystals by dissolving the precipitate in the smallest possible quantity of hot water and leaving the solution to evaporate over sulphuric acid. It dissolves in 11.5 pts. of water at  $15^\circ$ , and is but slightly more soluble in boiling water; in ether and alcohol it is quite insoluble even at the boiling heat (Hointz, *Ann. Ch. Pharm.* clvii. 291).

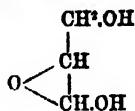
*Constitution of Hydracrylic acid.*—The formation of this acid from  $\beta$ -iodopropionic acid,  $CH^3I-CH^2-COOH$ , would lead to the inference that it is identical with ethylene-lactic acid,  $CH^2OH-CH^2-COOH$ . But hydracrylic acid, as already observed, is distinguished from all other modifications of lactic acid by being resolved when heated into water and acrylic acid. From ethylidene-lactic acid, it differs in not yielding iodoform by Lieben's reaction; and from ethylene-lactic acid—synthetically prepared by combining ethylene with carbonyl chloride, and decomposing the resulting chloride,  $CH^2Cl-CH^2-COCl$ , with an alkali (1st Suppl. 770)—it is distinguished by its products of oxidation. Ethylene-lactic acid is converted by oxidation with chromic acid, nitric acid, or melting potash, into malonic acid,  $COOH-CH^2-COOH$  (1st Suppl. 800); but hydracrylic acid when similarly treated yields totally different products (p. 717).

A further distinction between the two acids is afforded by the characters of their zinc salts, and zinc-calcium salts, those of hydracrylic acid being crystalline, as above stated, whereas those of synthetical ethylene-lactic acid are amorphous and never exhibit any sign of crystallisation. Lastly, hydracrylic acid or either of its salts, when heated with hydriodic acid, always reproduces  $\beta$ -iodopropionic acid (glycerin iodopropionic acid), 1 or 2 grams of substance being sufficient to exhibit the reaction; but synthetical ethylene-lactic acid, when similarly treated even in twenty times that quantity, does not yield a trace of  $\beta$ -iodopropionic acid.

The easy resolution of hydracrylic acid into water and acrylic acid shows that it is very nearly related to acrylic acid, acrolein and allyl alcohol. These compounds are now generally represented by the following formulæ (pp. 27, 47):

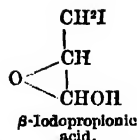
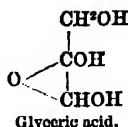
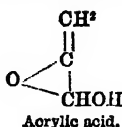
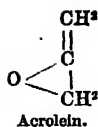
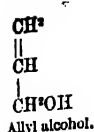


They do not contain the group  $CH^3$ , which therefore cannot be present in hydracrylic acid, and this conclusion is confirmed by the fact that this acid does not yield acetic acid by oxidation, or iodoform by Lieben's reaction. Hydracrylic acid must therefore contain the group  $CH^2OH$ , which exists also, together with  $COOH$ , in ethylene-lactic acid. Consequently hydracrylic acid cannot contain this latter group, since if it did both acids would be represented by the formula  $CH^2OH-OH^2-COOH$ , that is to say, they would be identical. It appears, therefore, very probable that hydracrylic acid has the constitution represented by the formula:



A compound thus constituted will be an acid: for organic hydroxides are converted into acids, not only by transformation of the group  $CH^2OH$  into  $COOH$ , but also when negative elements or radicals accumulate near an alcoholic hydroxyl.

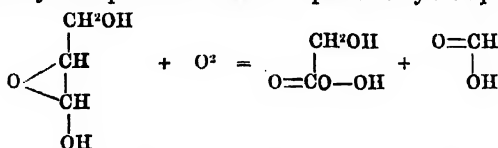
Admitting, then, this formula for hydracrylic acid, the compounds related to it must be constituted as follows:



These formulæ are preferable to those hitherto adopted, for the following reasons: When an alcohol undergoes oxidation, the oxygen which enters it is attracted by that carbon-atom which is already combined with oxygen. Now in glycerin,  $\text{CH}^2\text{OH}-\text{CHOH}-\text{CH}^2\text{OH}$ , each atom of carbon is already combined with oxygen, and therefore the oxygen which replaces the hydrogen will be as strongly attracted by one of the external carbon-atoms as by the middle ones, and thus glyceric acid will have the constitution above indicated.

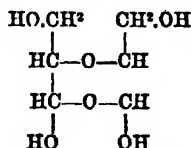
Acrolein, although possessing most of the properties of the aldehydes, differs from them by not uniting with alkaline bisulphites, and by its reaction with ammonia; it may therefore be expected to differ from the aldehydes in constitution. Its reduction to allyl alcohol and oxidation to acrylic acid are explained by the new formula as clearly as by the old one. When allyl alcohol is oxidised, it yields acrolein; in this case the oxygen is attracted, not only by the group  $\text{CH}^2\text{OH}$ , but likewise by the second atom of carbon: for it is well known that in the oxidation of carbon-compounds which have some of their carbon-atoms united by two combining units, the oxygen most readily attacks the carbon-atoms thus doubly united.

Hydracrylic acid is much more easily oxidised than any other modification of lactic acid, giving off torrents of carbon dioxide and a strong smell of formic acid. The oxidation probably takes place in the manner represented by the equation:



the first products being glycollic and formic acids, which are then further oxidised to carbonic and oxalic acids. The formation of acetic acid with only a little glycollic acid, by the action of melting potash, may be explained by supposing that, before the oxidising action of the potash begins, a large quantity of hydracrylic acid is converted into acrylic acid, which, as the temperature rises, is resolved into formic and acetic acids, while the glycollic acid is formed from unaltered hydracrylic acid.

The existence of the double hydracrylate of zinc and calcium suggests the idea that hydracrylic acid may be bibasic and polymeric with lactic acid. In this case its formula may be:



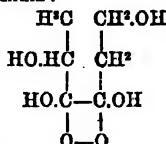
The question as to its molecular weight cannot be decided by the density of its ethylic ether, as this compound is decomposed by heat.

3. *Sarcrolactic acid*.—The sarcrolactates exhibit in many respects the characters of double salts of ethylidene- and ethylene-lactic acids. According to Wislicenus (*Deut. Chem. Ges. Ber.* ii. 619), the zinc salt of sarcrolactic acid is resolved by strong alcohol into a sparingly soluble crystalline salt and an easily soluble amorphous salt. The latter, so far as it could be examined, agreed in character with that of the acid prepared from  $\beta$ -iodopropionic acid, that is to say, with the hydracrylate. The sparingly soluble zinc salt, on the other hand, is not identical with the ethylidene-lactate, but contains 2 mol. water of crystallisation (instead of 3 mol.) Moreover the acid separated from this zinc salt differs from all the other modifications of lactic acid in being active to polarised light; it turns the plane of polarisation to the right ( $\alpha=3.5^\circ$ ), but its salts exert a levorotatory power ( $\alpha=-8.37^\circ$ ).

The presence of this optically active acid renders the sarcrolactates themselves optically active, whereas the double salts formed by direct mixture of ethylidene- and ethylene-lactates are optically inactive. There are also, as Heintz has pointed out (*Ann. Ch. Pharm.* clvii. 314), other particulars in which the sarcrolactates

differ from the corresponding artificially prepared double salts. Zinc sarcosylactate gives off its water at  $100^{\circ}$ , much more slowly than the artificially prepared double salt: it can also be recrystallised from water without sensible alteration of its composition, whereas the artificial double salt cannot. From the latter, indeed, it is easy, by repeated crystallisation, to obtain pure ethylidene-lactate of zinc, whereas when a solution of the sarcosylactate from which half the zinc has been precipitated by hydrogen sulphide is left to evaporate, unaltered sarcosylactate crystallises out, and the mother-liquor when saturated with zinc oxide yields the same salt. In the crystallisation of zinc sarcosylactate, it often happens that, after part of the salt has separated out, the whole solidifies to a translucent jelly, in which the microscope shows the presence of small elongated six-sided tables and long very slender flexible needles. This appearance is never exhibited by the artificially prepared double salt.

For these reasons Hantzsch regards sarcosylactic acid as a distinct modification of lactic acid, and proposes for it the formula :



If, on the other hand, sarcosylactic acid be regarded as a mixture or compound of an ethylidene- and an ethylene-lactic acid, one of which is optically active, then there will be four modifications of lactic acid, viz.:

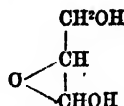
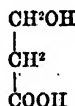
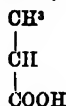
Inactive ethylidene-lactic acid,

Inactive ethylene-lactic acid,

Active ethylidene- or ethylene-lactic acid (paralactic acid),

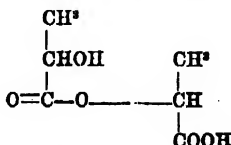
Hydracrylic acid :

whereas there are only three constitutional formulæ by which these modifications may be represented, viz.:



There is, however, good reason for supposing that the difference of structure between optically active bodies and their inactive isomerides—as, for example, in the several modifications of tartaric acid—is rather physical than chemical; in other words, that it depends on difference of arrangements of the molecules amongst themselves rather than on that of the atoms within the molecules. On this view the existence of the four modifications of lactic acid above-mentioned presents no anomaly.

**Lactic Anhydrides** (Wislicenus, *Ann. Ch. Pharm.* clxiv. 181). When pure aqueous lactic acid is left for several months over sulphuric acid in a vacuum, it is found that, notwithstanding the loss of weight which occurs from abstraction of water, the quantity of alkali required to neutralise a given weight of the aqueous acid continually diminishes; moreover, that the neutralised liquid, if made blue by addition of litmus, becomes red after a while, and if the free acid be again neutralised with alkali, the liquid again assumes a red colour after standing, and so on for several alternations. These results are due to the formation of dilactic acid,  $\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ}$ , which, as formerly shown by Wislicenus and van der Bruggen (*1st Suppl.* 772), may be regarded as an ethereal derivative of two molecules of lactic acid, one of which plays the part of an acid, the other that of an alcohol, its constitutional formula being



It is, therefore, at once a monobasic acid, a monosacid secondary alcohol, and a compound ether. Accordingly it will in the first instance be neutralised by 1 molecule of sodium hydrate; but the resulting sodium salt, like all compound ethers, will be partially decomposed by the water, and the free lactic acid thus produced will destroy the neutral reaction. If the decomposition has been complete, as for example when the



salt is quickly saponified by boiling with alkali, the neutralisation of the acid subsequently set free will require a quantity of base equal to that required for the first saturation.

It follows from these facts that when a solution of lactic acid is left to evaporate, dilactic acid forms in it even before all the water has evaporated, the quantity of the dilactic acid increasing as that of the water diminishes. Pure lactic acid, answering to the formula  $C^3H^5O^3$ , cannot therefore be obtained.

Further, when lactic acid is left at ordinary temperatures in an atmosphere kept constantly dry, the dehydration does not stop at the formation of the first anhydride—viz. dilactic acid, but proceeds to the formation of lactide,  $C^3H^4O^2$ . At higher temperatures, even in an atmosphere not perfectly dry, the dehydration goes on at an accelerated rate. This is shown by the following numbers, which represent the results of an experiment made with lactic acid which had stood for two months in the exsiccator (called in the table 'original acid').

	Water	Lactic acid	Dilactic acid	Lactide	Total
1. Original acid . . . . .	26.23	69.59	4.18	—	100 .
2. After 2 hours in the water-bath . . . . .	—	44.93	55.11	—	100.04
3. After 16 hours in the water-bath . . . . .	—	30.00	71.40	—	101.40
4. After 15 hours at $140^{\circ}$ – $150^{\circ}$ . . . . .	—	—	52.61	47.61	100.12
5. The resulting distillate . . . . .	4.65	43.87	51.48	—	100

The acid which had remained for 16 hours over the water-bath appeared also to contain lactide; as, when more strongly heated, it yielded a sublimate of crystalline lactide, even before the temperature had reached  $140^{\circ}$ .

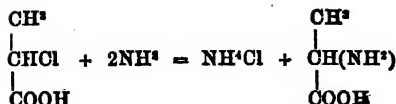
**Salts of Dilactic acid.**—Wislicenus observed several years ago that the crude product obtained by heating lactic acid to  $150^{\circ}$  gave, when neutralised with magnesia, instead of the crystalline lactate of magnesium, an amorphous saline mass consisting of magnesium dilactate. He has lately obtained and analysed the corresponding sodium salt, which is also an amorphous viscid mass. On the ethers of dilactic acid, see 1st Suppl. 773.

**Action of water on Dilactic acid.**—The conversion of this body into lactic acid by water at ordinary temperatures takes place very slowly. When 5 grams of a dehydrated product containing 89.86 p.c. of dilactic acid and 10.16 p.c. lactide were dissolved in 10 c.c. of absolute alcohol, precipitated by water, and the whole left to itself, the viscid precipitate did not disappear completely in six months, although it diminished considerably.

**Dihydracrylic acid,  $C^3H^4O^3$ .**—When crude hydracrylic acid, prepared according to Beilstein's directions, is carefully neutralised with sodium carbonate, there is obtained—besides the principal product, viz. sodium hydracrylate,  $C^3H^3NaO^3$ , which crystallises readily from alcohol—a small quantity of residue very slightly soluble in alcohol, and consisting of the sodium salts of three acids, which may with some difficulty be partially separated one from the other. One of these salts is, very deliquescent, quite insoluble in alcohol, and gives with solutions of calcium, barium, zinc, iron, copper, silver, lead, &c., amorphous, absolutely insoluble, precipitates. The copper, silver, lead, and barium salts agree with the formula  $C^3H^2M^2O^4$ . The acid is therefore bibasic and isomeric with adipimalic acid (p. 29). Wislicenus designates it as paradipimalic acid.

The sodium salts of the other two acids are easily soluble in dilute alcohol, very sparingly soluble, but in various degrees, in strong alcohol. The more soluble of the two is sodium acrylate; the other has the formula  $C^3H^2Na^2O^4$ . The acid of this latter salt, isomeric with dilactic and paradipimalic acid, is called by Wislicenus, dihydracrylic acid. Heated to  $120^{\circ}$  with hydriodic acid of sp. gr. 1.6, it is converted, like hydracrylic and acrylic acids, into  $\beta$ -iodopropionic acid; paradipimalic acid does not exhibit this transformation. The sodium salt of dihydracrylic acid is more permanent in the air than that of paradipimalic acid, and gives no precipitates with calcium or barium salts, but with lead salts it forms a precipitate soluble in excess of the precipitant (Wislicenus, *Deut. Chem. Ges. Ber.* iii. 809; *Ann. Ch. Pharm.* clxvi. 3; *Chem. Centr.* 1873, 331).

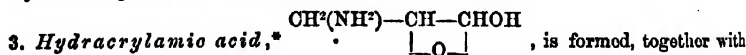
**Lactamic Acids** (Heintz, *Ann. Ch. Pharm.* clv. 25). 1. *Ethylidene-lactamic acid* or *Alanine*, which is a derivative of fermentation lactic acid, is formed, together with lactic acid, by boiling  $\alpha$ -chloropropionic acid with aqueous ammonia—  
2nd Sup.



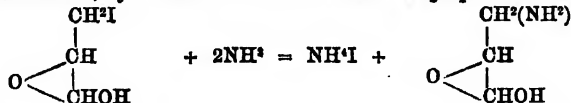
2. *Ethylidene-dilactamic acid*, or simply *Dilactamic acid*,  $\text{C}^6\text{H}^{11}\text{NO}^4$ , is formed when, in preparing alanine by Strecker's method, viz. by heating aldehyde-ammonia with hydrocyanic acid and excess of hydrochloric acid (i. 63), the hydrochloric acid is added first, and the hydrocyanic acid afterwards. The chlorine having been removed in the usual manner by lead hydrate and the lead by hydrogen sulphide, any alanine that may have formed, precipitated by alcohol and ammonia, and the alcohol volatilised, the liquid is boiled with barium hydrate, the barium exactly precipitated by sulphuric acid, and the filtrate boiled with cupric oxide. The blue-green solution, when left to evaporate, deposits indistinctly crystalline grains, which, when purified by washing with alcohol and recrystallisation, have the composition of *cupric dilactamate*,  $\text{C}^6\text{H}^8\text{NO}^4\text{Cu}$  (at  $110^\circ$ ). This salt does not dissolve very easily in water, is nearly insoluble in alcohol, and does not appear distinctly crystalline, even under the microscope. When dried at  $110^\circ$  it loses 15.52 to 17.01 p.c. water, and therefore probably crystallises with 3 mol. water. It is very different from the copper salt of alanine.

*Dilactamic acid* separated from the copper salt by hydrogen sulphide, crystallises from a concentrated aqueous solution in very slender microscopic needles, from the alcoholic solution in larger needles. It dissolves easily in water, less easily in aqueous alcohol, not at all in absolute alcohol.

The formation of dilactamic acid is accompanied by that of other substances, probably including trilactamic acid.



dihydracrylamic acid, by the action of ammonia on  $\beta$ -iodopropionic acid:



The two acids may be separated by repeatedly boiling down the solution with lead oxide, as long as ammonia continues to escape, exhausting the residue with water, which leaves a residue of basic lead iodide, and adding alcohol, which precipitates the lead-salt of dihydracrylamic acid in colourless needles, while the hydracrylamate remains in solution.

A better method of separation, however, is to convert the two acids into the silver-salts. To effect this, the iodine and ammonia are removed as above described, and the lead is precipitated from the solution by sulphuretted hydrogen. By adding silver oxide to the filtrate, as long as silver dihydracrylamate is formed—a salt which is almost insoluble in water—and passing sulphuretted hydrogen through the filtrate, a solution of hydracrylamic acid is obtained. This solution, when evaporated, leaves the acid as a syrupy liquid, which, by agitation with ether and repeated boiling of the residue with alcohol, is converted into a solid mass.

Hydracrylamic acid is readily soluble in water, but nearly insoluble in absolute alcohol. It crystallises in transparent prisms, belonging probably to the monoclinic system. On heating it to  $170^\circ$ , it turns brown, and sublimes very slowly in feathery needles; at a higher temperature it is completely decomposed, leaving a very difficultly combustible charcoal. It has a sweetish taste; the faint acid reaction of its concentrated solution is probably due to the presence of a little dilactamic acid. It combines with bases as well as with acids.

The *copper salt*  $(\text{C}^4\text{H}^4\text{NO}^2)^2\text{Cu} + 5\text{H}_2\text{O}$ , which is much more soluble in water than the corresponding alanine compound, crystallises in large dark-blue rhombic prisms. With *silver nitrate* the acid yields the compound  $\text{C}^4\text{H}^4\text{NO}^2\cdot\text{AgNO}^3$ , in colourless needles, which decompose on heating.

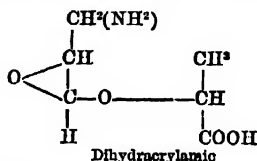
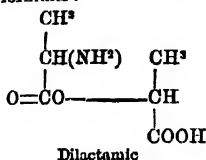
4. *Dihydracrylamic acid*,  $\text{C}^6\text{H}^{11}\text{NO}^4$ , obtained by decomposing its lead or

\* In Heintz's paper this acid is called *ethylene-lactamic* or *paralactamic acid*, and represented by the formula  $\text{CH}^2(\text{NH}^2) - \text{CH}^2 - \text{COOH}$ ; but according to the explanations already given of the constitution of  $\beta$ -iodopropionic acid and its derivatives, it must be hydracrylamic acid.

silver salt with sulphuretted hydrogen, remains on evaporation as a thick, colourless syrup gradually solidifying on standing to a radiate crystalline mass. Once, by adding a particle of the solid acid to a concentrated solution, distinct crystals were obtained consisting of shining plates or flat needles.

If, to the solution saturated with ammonia, silver nitrate is added, a precipitate of silver dihydracrylamate,  $C^4H^7N^2O^4Ag^2$ , is obtained. On adding more silver nitrate to the filtrate whilst warm, the compound  $C^4H^7N^2O^4Ag^2 + 1\frac{1}{2}H^2O$  separates on cooling in colourless crystals. When ammonia is added to its solution, silver dihydracrylamate is precipitated.

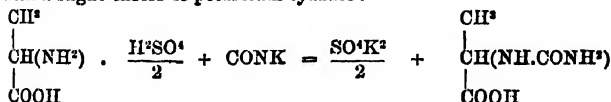
According to the formula of dilactic acid suggested by Wislicenus (p. 720), dilactamic and dihydracrylamic acids may perhaps be represented by the following constitutional formulae:



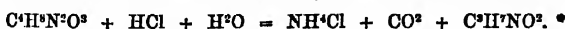
#### LACTIC FERMENTS. See FERMENTS.

**LACTONIC ACID**,  $C^4H^5O^4$ , syn. with *Isodiglycol-ethylenic acid* (iii. 414). This acid, produced by treating milk-sugar with bromine, and the product with silver oxide, is regarded by Fittig as monobasic, and by Hlasiwetz as dibasic, for reasons similar to those adduced with reference to gluconic acid,  $C^6H^{12}O^7$  (p. 560). The so-called basic calcium and barium salts,  $C^4H^5CaO^4$  and  $C^4H^5BaO^4$ , are produced in the same manner as the corresponding gluconates.

**LACTURAMIC ACID**,  $C^4H^7N^2O^3 = CH^3-CH(NH.CONH^3)-COOH$  (Urech, *Ann. Ch. Pharm.* clxv. 99). This acid is formed by heating alanine sulphate in aqueous solution with a slight excess of potassium cyanate:

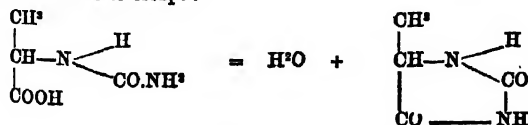


On adding a large quantity of alcohol, removing the potassium sulphate by filtration, evaporating, and crystallising the product several times from alcohol, lacturamic acid is obtained as a white indistinctly crystalline mass, slightly soluble in cold alcohol, insoluble in ether, melting with decomposition at  $155^\circ$ . Heated with hydrochloric acid in a sealed tube, it is resolved into alanine, carbon dioxide and ammonia:



Silver lacturamate,  $C^4H^7N^2O^4Ag$ , obtained by adding silver nitrate to a moderately dilute solution of the acid neutralised with sodium carbonate, crystallises gradually in needles grouped in tufts or double wedges, anhydrous and somewhat sparingly soluble in water. The lead salt  $(C^4H^7N^2O^4)^2Pb + 2H^2O$  is obtained in colourless crusts by boiling the aqueous acid with excess of lead carbonate, and leaving the filtrate to evaporate. The copper salt, obtained by saturation, forms a blue solution which dries up under the exsiccator to an emerald-green mass.

**LACTYL-UREA**,  $C^4H^7N^2O^2$ , is produced by heating lacturamic acid to  $140^\circ$  as long as water continues to escape:



The decomposition is precisely analogous to that by which hydantoin,  $C^3H^5N^2O^2$ , the next lower homologue of lactyl-urea, is formed from acetyl-uramic acid. (Urech.)

Lactyl-urea is also formed in the preparation of alanine from aldehyde-ammonia by Strecker's method, when potassium cyanide is used instead of hydrocyanic acid (Heintz, *Ann. Ch. Pharm.* clxix. 120). For this purpose hydrochloric acid is added to aldehyde-ammonia and potassium cyanide dissolved in water, and after some days the solution is evaporated in order to allow ammonium chloride and potassium chloride to separate.

The syrupy liquid is treated with ether-alcohol to dissolve the alanine, and after the removal of the alcohol and ether by distillation, the substance is saturated with ammonia. The addition of alcohol now causes the separation of alanine contaminated with sal-ammoniac, and the alcoholic liquid separated from this contains lactyl-urea, together with several other substances. The lactyl-urea may be separated as follows:—The potash and ammonia are precipitated by sulphuric acid, after which the alcohol is removed by distillation, and the chlorine is separated by silver hydrate, the excess of silver being then thrown down by sulphydric acid. After the small remaining portion of ammonia has been removed by boiling with baryta, and the baryta by sulphuric acid, a syrupy residue is obtained on evaporation. This syrupy liquid dissolves in alcohol, from which it separates on addition of ether. The alcoholic filtrate separated from this syrup is freed from alcohol by distillation, and the acid residue neutralised with lime. Lactyl-urea is then deposited in long needles which, when purified by crystallisation and pressure, are converted into large colourless rhombic prisms, efflorescing in the air, and containing  $C^4H^5N^2O^2 + H^2O$ . When deposited from a strong hot solution it forms anhydrous microscopic needles. Its formation in this reaction is due to the presence of cyanate in the potassium cyanide employed, considerable quantities of it being formed when a solution containing potassium cyanate, potassium cyanide, and aldehyde-ammonia is treated with dilute sulphuric acid.

Lactyl-urea crystallises in cauliflower-like tufts, easily soluble in water, insoluble in ether; it melts at  $140^\circ$  (Heintz),  $125^\circ$  (Urech), and sublimes slowly at a somewhat higher temperature, the melted mass becoming brown at the same time. Its taste is bitter; it is easily soluble in water or alcohol, less soluble in ether, and it is neutral to litmus. When it is heated to  $100^\circ$ – $145^\circ$  with barium hydrate, much ammonia is evolved, and the residue contains alanine and barium carbonate. A similar decomposition takes place when lactyl-urea is boiled for a very long time with baryta-water; but when it is boiled with baryta-water for half an hour only, barium lactamate is formed.

Lactyl-urea treated with silver hydrate forms the compound  $C^4H^5AgN^2O^2$ , almost insoluble in water, but soluble in ammonia, and precipitated as a white powder from its ammoniacal solution by nitric acid. Lactyl-urea does not appear to combine with silver nitrate (Heintz).

**LANARKITE.** This mineral, from Leadhills in Scotland, was examined more than fifty years ago by Brooke, and more recently by Thomsen, both of whom regarded it as a compound of sulphate and carbonate of lead (iii. 467). But recent analyses by Pisani (*Compt. rend.* lxxvi. 114) and by Maskelyne a. Flight (*Chem. Soc. J.* [2], xii. 103), have shown that it contains no carbonic acid, but is a compound of sulphate and oxide:  $PbSO^4.PbO$ .

	Pisani	Maskelyne a. Flight	Calculation
Sulphate . . .	54.17	57.70	57.605
Oxide . . .	43.66	42.89	42.395
	97.83	100.59	100.000

The older analyses were probably made upon a different mineral.

**LANTANURIC ACID.** On the compound thus designated by Schlieper, see ALLANTOÏN (p. 45).

**LANTHANUM.** For Mendelejeff's views regarding the atomic weight of this metal, see CERITE METALS (p. 273).

For Erk's method of separating lanthanum from didymium, see DIDYMIUM (p. 428).

**LANTHOPINE.** One of the bases obtained by Hesse from the aqueous extract of opium. See 1st Suppl. 774; also OPIUM-BASES in this volume.

**LANUGINIC ACID,  $C^{10}H^{10}N^{10}O^{20}$ .** An acid produced by the action of alkalis upon wool. When wool purified by treatment with alcohol, ether, and boiling acetic acid is boiled with concentrated baryta-water, the excess of baryta removed by carbonic acid, the filtrate precipitated by lead nitrate, and the copious precipitate washed and decomposed by hydrogen sulphide, the solution on evaporation leaves lanuginic acid as a yellowish, translucent, uncrystallisable mass. Its barium salt is  $C^{10}H^{10}N^{10}O^{20}.Ba$ ; lead salt,  $C^{10}H^{10}N^{10}O^{20}.Pb$  (P. Champion, *Compt. rend.* lxxii. 380).

**LAUDANINE, LAUDANOSINE.** Bases obtained by Hesse from the aqueous extract of opium. See 1st Suppl. 774, and OPIUM-BASES in this volume.

**LAURYLENE.** The terpene from Bay-oil. See OILS, VOLATILE.

**LAWROWITE.** This mineral, described by Kokscharow (1st Suppl. 775),

occurs in crystalline grains, together with small druses of vanadiolite, in quartz, on a vein of limestone in the valley of Slüdänka (or Sludjanka) near Lake Baikal. Lawrowite is cleavable parallel to the faces of a prism of  $87^\circ$ ; hardness 5; sp. gr. 3.04. Vanadiolite has a conchoidal fracture, blackish-green colour, greyish-green in the streak, translucent on the edges, and melts with intumescence to a black slag. Both are mixtures of augitic substance with (so-called) calcium hypovanadate, lawrowite being a grass-green diopside containing 4.20 p.c. of that salt as pigment, while vanadiolite contains 1 mol. of the hypovanadate to 3 mol. of augitic substance:—

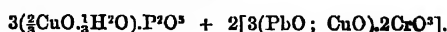
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeO}$	$\text{CaO}$	$\text{MgO}$	$\text{X}^*$
Lawrowite	53.65	2.25	2.48	23.05	16.00	2.57 = 100
Vanadiolite	15.61	1.10	1.40	34.43	2.61	44.85 = 100

(R. Hermann, *J. pr. Chem.* [2], i. 442).

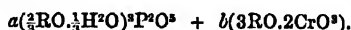
**LAXMANNITE.** A mineral occurring at Beresowsk in Siberia. Hardness = 3. Sp. gr. = 5.77. Colour, olive-green. Two analyses by Nordonskiöld (*J. pr. Chem.* cv. 335) gave—

$\text{PbO}$	$\text{CuO}$	$\text{Fe}^2\text{O}^3$	$\text{Cr}^2\text{O}^3$	$\text{P}^2\text{O}^5$	$\text{H}^2\text{O}$
61.26	12.43	1.09	15.26	8.05	1.31 = 99.40
61.06	10.85	1.28	16.76	8.75	0.90 = 99.60

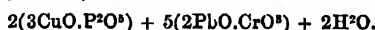
whence Nordonskiöld deduces the formula—



He supposes that the  $\text{P}^2\text{O}^5$  and  $\text{CrO}^3$  in this mineral are isomorphous, and thence deduces the general formula—



R. Hermann (*ibid.* [2], i. 447) deduces from Nordonskiöld's analysis the formula—



He moreover regards laxmannite as identical with vauquelinite (i. 934), assuming that Berzelius overlooked the phosphoric acid in the latter.

**LEAD.** *Occurrence.*—On Antimonite and Antimonate of Lead occurring at Constantine in Algeria, see NADONITE.

On native Molybdates and Vanadates of Lead, Eosite, Dechonite, Descloizite, &c., see MOLYBDATES and VANADATES.

**Metallurgy.** The extraction of lead from galena in reverberatory furnaces at 'Nouvelle Montagne' is described by V. Bouly (*Ann. Min.* [6], xvii. 159; *Jahresb. f. Chem.* 1870, 1076).

*Lead Fume.*—C. P. Williams (*Chem. News*, xxiii. 236) has analysed the fumes condensed in the flues of furnaces in which lead ores containing zinc are smelted: I. So-called 'Bartlett Lead-white.' II. Zinc-white from the ore of Sinking Valley in Pennsylvania. III. From Wisconsin ore worked for the preparation of zinc-white at Birmingham in Pennsylvania.

	I.	II.	III.
ZnO . . .	72.083	73.246	9.23
PbO . . .	0.274	—	13.21
Sb <sup>2</sup> O <sup>3</sup> . . .	trace	—	—
Fe <sup>2</sup> O <sup>3</sup> . . .	trace	—	trace
PbSO <sup>4</sup> . . .	23.968	25.084	74.05
ZnSO <sup>4</sup> . . .	0.810	0.574	trace
ZnCl <sup>2</sup> . . .	0.839	—	—
Fe <sup>2</sup> Cl <sup>3</sup> . . .	0.071	—	—
SbCl <sup>3</sup> . . .	trace	—	—
CdCl <sup>2</sup> . . .	0.256	—	—
CdSO <sup>4</sup> . . .	—	0.187	—
CaCO <sup>3</sup> . . .	—	0.729	3.27
SO <sup>2</sup> . . .	—	—	0.84
Lead in total . . .	16.624	17.132	62.840
Silver " . . .	0.0087	0.014	0.0019

Williams proposes to condense such fumes in chambers through which water falls in the form of rain (compare iii. 523–526).

\* Hypovanadic oxide,  $\text{V}^2\text{O}^4 \cdot 2\text{V}^2\text{O}^4$ .



Historical notices of the process of desilvering lead with zinc have been given by Gruner (*Berg. u. Hüttenm. Zeitung*, 1870, 190) and by Balling (*Dingl. pol. J.* cxviii. 52).

**Estimation.** F. H. Storer (*Bull. Soc. Chim.* [2], xiv. 213), estimates the amount of lead in galena and other compounds by decomposing the compound with hydrochloric acid in presence of zinc, whereby hydrogen sulphide and metallic lead are produced. The same decomposition may be effected by hot oxalic acid, acetic acid, and dilute sulphuric acid. Dilute nitric acid, on the other hand, even at ordinary temperatures, forms free sulphur and nitrate of lead. Decomposition with hot hydrochloric acid is the best process for estimating the lead and sulphur, especially for the variety of galena occurring in America, which contains no heavy metal except lead. 2 or 3 grams of the finely-pounded ore are placed in a beaker, together with a zinc regulus 1 inch in diameter and  $\frac{1}{4}$  inch thick, and treated with 100 to 150 c.c. of dilute hydrochloric acid (1 vol. acid to 4 vol. water), the liquid being heated to 40°–50°, and the vessel is covered with a watch-glass and set aside for 15 to 20 minutes. After the liquid has become clear and no more hydrogen sulphide is evolved, the solution is poured upon a moderately large filter of smooth paper on which rests a piece of zinc; the lead thereby precipitated is washed with water, and introduced into a tared porcelain crucible, the zinc being cleansed with a glass rod or a piece of caoutchouc. The lead is then dried at a moderate heat in a stream of coal-gas. The amount of sulphur in the galena is estimated by arresting the escaping hydrogen sulphide in the usual way. If the galena is mixed with insoluble matrix, the lead after weighing is to be dissolved in dilute nitric acid, and the residue weighed. The same method of analysis may be applied to the sulphate, chromate, nitrate, carbonate, and other compounds of lead. Attempts to estimate the lead and sulphur in galena by means of nitric acid and zinc did not give satisfactory results.

Mascazzini (*Dingl. pol. J.* cxvii. 46) describes a new method of assaying lead ores based upon the conversion of the lead into sulphate by heating with ammonium sulphate. Lead ores which are all but free from other metals may be reduced directly by means of nascent hydrogen (the zinc should be finely pulverised) and subsequent fusion into a button of lead. Ores containing blende or pyrites must first be converted into sulphates by means of ammonium sulphate. The quantity of salt required varies with the percentage of metallic sulphides present. Two parts by weight of the dry sulphate usually suffice for the conversion of the richest ores into sulphates. The mixture of ore and ammonium salt is heated in a porcelain crucible covered with a small inverted dish. As soon as the boiling up has ceased, the temperature can be increased to strong red heat, without risk of losing any substance from spitting, till the ferric and cupric sulphates undergo decomposition. The mass when cold is readily dissolved out with hot water acidulated with a little sulphuric and hydrochloric acid. The latter prevents the silver from passing into solution, especially if the liquid be diluted and allowed to stand for some time. The insoluble portion, consisting of lead sulphate and silver chloride, is removed by decantation and filtration, and is well washed with hot water, dried, removed to a flask, and treated with powdered zinc and hydrochloric acid as long as any reduction takes place. Two parts by weight of zinc are generally sufficient to reduce one part of pure galena, provided both the metallic zinc and lead sulphate be in the state of a fine powder and intimately mixed. Since even the best kinds of zinc contain a little lead, it is necessary to determine the amount of lead so present, and to make allowance for it. The spongy mass of reduced metals is washed with water freed from air, or with water acidulated with a little dilute sulphuric acid; it is next transferred to a flat basin, pressed with a flattened glass rod, and thoroughly washed. The mass is then introduced into a crucible, dried at a gentle heat, and mixed with  $1\frac{1}{2}$  to twice its weight of a reducing flux, covered with a thin layer of the same, or a little dry sodium chloride, and fused by raising the temperature gradually to a red heat.

A flux proposed by Plattner, consisting of 13 parts by weight of potassium carbonate, 10 parts by weight of dry sodium carbonate, 5 parts of fused borax, and 5 parts of dried starch effects the fusion readily, and yields a clean metallic button.

The same process is applicable to the analysis of white lead, minium, and litharge, of lead ores containing gold and silver, and by somewhat modifying the fluxes, also to the estimation of antimony, tin, and copper. Should the gold or silver ores be deficient in lead, a quantity of litharge or lead salt is added, sufficient to yield a proper regulus.

**Separation of Lead from Zinc.**—The separation of these metals in galena and blende may be effected by heating the finely powdered mineral with excess of iodine to 200° in a sealed tube for several hours, then breaking the tube, pulverising the contents, boiling the powder with distilled water till the excess of iodine has disappeared, then leaving it to cool and filtering. Zinc and iron are thereby dissolved as iodides,

while the lead remains on the filter as iodide together with sulphur and matrix. The lead iodide may be extracted from this mixture by hot water (Filhol a. Mellies, *Ann. Chim. Phys.* [4], xxii. 64).

*Analysis of Soft Lead.*—The following method is given by Fresenius (*Zeitschr. anal. Chem.* viii. 148; *Zeitschr. f. Chem.* 1870, 55; *Jahresb. f. Chem.* 1870, 906): 1. The lead having been scraped clean with a knife, two pieces weighing 200 grams each are treated with dilute nitric acid, which dissolves the lead completely, excepting when antimony is present, in which case the solution must be filtered and the undissolved oxide mixed with the subsequent antimony precipitations. The solution of one portion is diluted to 1500 c.c. and mixed with 1 c.c. of hydrochloric acid, sp. gr. 1.12, previously diluted with about 50 c.c. of water. This quantity is too small to produce a precipitate of lead chloride; silver, if present, is deposited as chloride after two or three days standing, and after the liquid has been siphoned off, may be collected on a filter, washed, and weighed. The solution of the second portion of lead is mixed in a 2-litre flask with about 115 grams of pure strong sulphuric acid, and diluted up to the mark with water. As soon as the liquid above the precipitate has become clear, 1750 c.c. are measured off and evaporated till fumes of sulphuric acid are abundantly given off; the residue after cooling is mixed with 60 c.c. water; and the solution is filtered from the separated lead sulphate. This precipitate is to be dissolved in hydrochloric acid, the solution precipitated with hydrogen sulphide, the precipitate digested with potassium sulphide, and the resulting solution tested for antimony by acidulation with hydrochloric acid. The sulphuric solution diluted and warmed is treated with hydrogen sulphide; the liquid, after standing for twelve hours, is filtered off at a gentle heat; the precipitated sulphides are digested with potassium sulphide; the resulting solution acidulated with hydrochloric acid; and the sulphides of antimony and arsenic thereby precipitated are added to those previously obtained.

The precipitate insoluble in potassium sulphide is treated with dilute sulphuric acid, and the solution is evaporated with addition of sulphuric acid, filtered from the separated lead sulphate, neutralised with potash, and mixed with sodium carbonate and a little potassium cyanide. On gently heating the liquid, bismuth oxide is precipitated, which, after washing, may be dissolved in acid, precipitated with ammonium carbonate, and weighed.

The solution containing the potassium cyanide is tested with a few drops of potassium sulphide for silver and cadmium. If a precipitate is formed, it must be dissolved in nitric acid, the silver precipitated by hydrochloric acid, and the cadmium, after concentration of the filtrate, with sodium carbonate. The solution freed from these two metals is to be acidulated and evaporated to expel hydrocyanic acid, and treated with hydrogen sulphide to precipitate copper; the precipitated sulphide is weighed; and the estimation (if the quantity is very small) checked by titration with potassium iodide, after solution in nitric acid and evaporation with sulphuric acid.

The precipitates of antimonious and arsenious sulphides are washed, dried and treated with carbon sulphide, then oxidised with fuming nitric acid, mixed with sodium carbonate and nitrate, dried and fused. The fused mass, after softening and trituration with water, is washed with a mixture of water and alcohol; the filtrate, after concentration, is heated with dilute sulphuric acid till all the nitric acid is expelled, and hydrogen sulphide is passed into it at 70°. The precipitate is exhausted with the smallest possible quantity of ammonium carbonate, the solution acidulated, a little sulphuretted hydrogen passed into it, and the resulting precipitate of arsenious sulphide dried at 100° and weighed. The result may be verified by Kessler's method of titration with chromic acid and ferrous sulphate (*Pogg. Ann.* xcv. 204). The precipitate is treated with a hydrochloric solution of mercuric chloride, whereby the arsenic is dissolved as arsenious acid:  $2\text{As}^{\text{S}} + 9\text{HgCl}_2 + 6\text{H}^{\text{O}} = 2\text{As}^{\text{O}} + 3(2\text{HgS}.\text{HgCl}_2) + 12\text{HCl}$ ; the resulting solution is mixed with a titrated solution of potassium chromate till a permanent yellow-green is produced; a titrated solution of ferrous sulphate is then added till a drop taken out gives a blue precipitate with dilute potassium ferricyanide; and finally chromic acid solution is very gradually added till the blue precipitate has disappeared, the solutions being of course so dilute that the green colour of the chromic oxide shall not interfere with the distinctness of the blue precipitation. On deducting the quantity of chromic acid solution equivalent to the ferrous salt added, from the total quantity of chromic acid solution used, the difference gives the amount of chromic acid expended in oxidising the arsenious acid.

The sodium antimonate, together with the antimonious sulphide left undissolved by the ammonium carbonate, is to be dissolved in hydrochloric acid; the antimony reprecipitated by hydrogen sulphide; and the precipitate dried in a stream of carbon dioxide. The result may be checked in the same manner as in the case of the arsenic precipitate.



The filtrate from the copper sulphide, after concentration, is made just alkaline with ammonia, mixed with ammonium sulphide, and set aside in a closed vessel for 24 hours. To obtain the last traces of nickel, the filtered solution is evaporated, after addition of a little acetic acid. The precipitate formed by the ammonium sulphide is treated several times with a small quantity of a mixture of 6 pts. sulphuretted hydrogen water and 1 pt. hydrochloric acid of sp. gr. 1.12, to dissolve zinc and iron. The sulphides of nickel and cobalt are dissolved in nitromuriatic acid, after the filter has been incinerated; and the solution, after evaporation, is mixed with ammonia to slight alkaline reaction, and filtered after addition of a small quantity of ammonium carbonate. The filtrate is boiled in a platinum crucible with potash as long as ammonia continues to escape; and the separated nickel oxide, after being weighed, is examined with the blow-pipe for cobalt.

The solution of zinc and iron is oxidised by nitric acid, the iron precipitated by ammonia, redissolved, reprecipitated, and weighed. For verification, the ignited oxide may be fused with acid potassium sulphate, reduced with zinc, and titrated with permanganate solution. The zinc is precipitated with ammonium sulphide, separated by dilute acetic acid from any manganese that may be present, and weighed. The result may be checked by titration with potassium ferrieyanide and permanganate. From the acetic solution after evaporation, the manganese may be precipitated by caustic potash.

In calculating the results of the analysis, account must be taken of the space occupied in the measuring vessel by the sulphate of lead. By repeated experiments Fresenius has found that for 200 grams of lead this space is equal to that of 45 grams of water at 16°. The quantities of metal determined in 1750 c.c. of solution must therefore be referred to the quantity of solution corresponding with 200 grams of lead, that is to say, 1955 c.c., or, as may be assumed for simplification, to 179 grams of lead employed.

By test experiments, Fresenius has shown that, in the determination of quantities of metal amounting to only a few milligrams, good volumetric methods are affected with errors of only 0.00005 to 0.0002 gram, whereas gravimetric methods requiring ignition of precipitates involve errors of 0.0002 to 0.0003 gram, and those which require the collection of precipitates on dried and weighed filters are liable to errors of 0.0003 to 0.0007 gram.

The table on p. 731 exhibits the quantities of foreign metals contained in a number of soft leads of recent production. Analyses 15-21 are by Fresenius, made by the method above described; the rest are by Hampe (*Preuss. Zeitschrift für Berg-, Hütten-, und Salinenwesen*, xviii. 195; *Chem. Centr.* 1871, 281), made by a similar method.

**Alloys of Lead** (A. Baur, *Deut. Chem. Ges. Ber.* iii. 691; iv. 449). An alloy of lead and platinum, PtPb, is obtained by fusing 3 parts of lead and 1 part of platinum, and exposing the very brittle pulverised mass, under a bell-jar, to the action of carbonic acid, oxygen, and acetic acid vapours. After three weeks the white lead formed is dissolved in acetic acid, the residue left to form more white lead, then again treated with acetic acid, and so on till no further action takes place; the alloy is then separated from finely divided platinum by levigation. As thus prepared it forms a crystalline powder, having a shining surface and steel-grey colour, easily decomposed by boiling with mineral acids, but not acted upon by dilute acetic acid. When heated it fuses quickly to a crystalline, very brittle, reddish mass, resembling bismuth. It may be obtained at once in this state by fusing platinum with a slight excess of lead under a covering of borax-glass. Chemical combination takes place readily, and is accompanied by vivid flashes of light. The crucible should be allowed to cool slowly (by being placed in hot ashes). The alloy may be freed from excess of lead by treatment with acetic acid and exposure to air as above. Its density is 15.736, the calculated density being—supposing no contraction to take place—14.89. An alloy containing two atoms of lead to one of platinum, is obtained by employing excess of lead. The alloy PtPb<sub>2</sub> differs but little from PtPb in its outward appearance.

An alloy of lead and palladium is obtained by fusing granulated lead in a porcelain crucible, with somewhat more than one part by weight of palladium foil. Combination takes place readily and is marked by flashes of light. The product is a beautiful, crystalline, brittle, greyish-white mass, which is freed from excess of lead by acting upon it with acetic and carbonic acids. It is attacked freely, sugar of lead and white lead being formed; and on powdering it very finely and exposing it repeatedly to the action of these acids, it was found that palladium even dissolved in acetic acid, and that the remaining alloy was of constant composition. This alloy, which has the composition Pd<sup>2</sup>Pb, forms a steel-grey, crystalline powder, difficultly fusible, and having a specific gravity of 11.225, theory requiring 11.65. When it was used as a negative electrode in a battery of six Bunsen elements, no occlusion of hydrogen could be traced.

No alloys of lead and gold, or of lead and silver, could be obtained by fusing together the respective metals.

An *amalgam of lead* is obtained by melting 2 parts of lead in a crucible, and gradually adding 1 part of mercury. The resulting amalgam is then acted upon with acetic and carbonic acids whilst exposed to air, as long as any sugar of lead and white lead is formed. It contains 40.86 of lead and 59.12 of mercury, the formula  $\text{Pb}^2\text{Hg}^2$  requiring 40.82 of Pb and 59.17 of Hg, and forms a compact, crystalline, granular white mass, of specific gravity 12.49 at 17°. The calculated density of an amalgam of  $\text{Pb}^2\text{Hg}^2$  is 12.6085 (sp. gr. of Hg = 13.557). Hence it follows that no contraction has taken place. This is quite in harmony with the observations made by Crookewitt (*Ann. Ch. Pharm.* lxxiii. 290) on amalgams of equal atoms of lead and mercury, but runs counter to the observations made by Kupffer on lead amalgams.

**Lead Chloride,  $\text{PbCl}_2$ .** The solubility of this compound in water and in aqueous hydrochloric acid was determined in 1868 by J. C. Bell (*1st Suppl.* 776; *Chem. Soc. J.* [2], xxi. 350), who found that pure water at 17.7° dissolves 0.046 part of it, or 1 part in 120; with the addition of 1 p.c. hydrochloric acid, only 0.347, while with 14 p.c. of the acid, only 0.000 is dissolved, which is the minimum quantity. After the liquid becomes more acidified, the solubility of the salt increases, so that at 72 p.c. of acid it is more soluble than in water, and in the pure acid (sp. gr. 1.162) as much as 2.900 is dissolved. The reaction is rather different when sodium chloride is used as a solvent. Field (*Chem. Soc. J.* [2], xi. 575), whose experiments also show that the solubility of lead chloride in pure water is 1 part in 120, finds that, on the addition of sodium chloride to the extent of 5 p.c., the solubility of the lead chloride decreases very considerably, and only 1 in 437 remains in solution. When, however, the lead salt is digested with a concentrated solution of sodium chloride, it is found to be rather less soluble than in water, viz., 1 in 129. This fact may be strikingly exemplified by the addition of solution of sodium chloride to an aqueous solution of lead chloride, when crystals of the latter are deposited, and *vice versa*, when water is added to a solution of lead chloride in concentrated sodium chloride.

It is well known that when lead sulphate is treated with hydrochloric acid, lead chloride is formed and free sulphuric acid remains in solution, and Field's experiments show that even a cold saturated solution of sodium chloride immediately decomposes lead sulphate. And it almost appears that at first there is not only an actual decomposition, but a solution, as 1 gram of lead sulphate dissolves perfectly in 100 grams of solution of sodium chloride, and after some hours deposits crystals of lead chloride. Sulphuric acid, or a soluble sulphate, gives no precipitate with lead chloride dissolved in sodium chloride.

The different forms of crystals of lead chloride observed by Mr. Bell, some being in fine needles and others in feathery plates, may be obtained in great beauty by the following method:—A solution of aniline hydrochloride forms lead chloride with difficulty; indeed, both solutions must be rather concentrated before any reaction is perceptible. On leaving the liquid to stand some time, fine needle-shaped crystals are deposited, and if to the mother-liquor a few drops of sodium chloride be added, a beautiful mass of iridescent scales is produced, differing entirely in physical structure from the former. When potassium iodide is added to a solution of lead chloride in sodium chloride, the precipitate formed is not amorphous, but has the brilliant spangly appearance which it presents when deposited from its solution in hot water.

When sodium chloride is added to either acetate or nitrate of lead, if the solutions be sufficiently concentrated, it is well known that a white precipitate is formed consisting of lead chloride. But if acetic acid be immediately added to the precipitate produced in the acetate solution, the whole is entirely dissolved for the moment, but crystals of lead chloride speedily begin to form; the precipitate in the lead nitrate solution remains unchanged on the addition of acetic acid. And further, if to the clear solution, after the precipitation of lead nitrate by sodium chloride, any acetate be added, even in the cold, a cloudiness is immediately formed which gradually becomes a precipitate. This is particularly the case with copper acetate, which, if agitated with the solution above referred to, yields in a few hours a copious deposit, perfectly soluble in acetic acid. The same reaction is produced by the formates (Field).

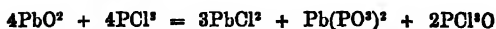
**Lead Oxides.** The monoxide,  $\text{PbO}$ , is completely reduced by carbon monoxide at the temperature of melting zinc (I. L. Bell, *Chem. News*, xliii. 258). It is not acted on by phosphorus trichloride at 160°, but when it is moistened with the trichloride and heated directly over a lamp-flame, a violent action takes place attended with flame and ignition, chloride and phosphite of lead being formed, and a large quantity of lead separated in the metallic state:



IMPURITIES IN SOFT LEADS.

	Name of Works	Year	Copper p.c.	Antimony p.c.	Iron p.c.	Zinc p.c.	Silver p.c.	Bismuth p.c.	Nickel p.c.	Cadmium p.c.
1	Villach . . . . .	1868	0.0021	0.0052	0.00250	0.0032	trace	not determined		
2	Friedrichshütte, Tarnowitz (before the intro- duction of desilverizing by zinc) . . . . .	"	0.0013	0.0022	0.0080		0.0015	"	"	
3	Bleiwerk in Belgum (as in 2) . . . . .	"	0.0014	0.0037	0.0016	0.0016	0.0008	"	"	
4	Panlehütte near Katowitz in Silesia (as in 2) . . . . .	"	0.0019	0.0013	0.0013	0.0014	0.0025	"	"	
5	Burgweyer Hütte (desilverized poor lead) . . . . .	"	0.006	0.002	0.004	0.003	0.0009	"	"	
6	Widow Blackett and Co. . . . .	"	0.0034	0.0046	0.0012	0.007	0.0035	"	"	
7	Joster, Blackett, and Wilson . . . . .	"	0.0526	0.0074	0.0015	0.0018	0.004	"	"	
8	Eythoren and Sons. . . . .	"	0.0094	0.0021	0.0016	0.001	0.00075	"	"	
9	Common-Lead Company . . . . .	"	0.0236	0.0058	0.0021	0.0018	0.001	"	"	
10	Pontifex and Wood . . . . .	"	0.0738	0.0032	0.0022	0.0032	0.002	"	"	
11	Mechnich . . . . .	"	0.0023	0.0031	0.0017	0.0026	0.0005	—	trace	—
12	Prath and Jung . . . . .	"	0.0034	0.0081	0.0013	0.0009	0.0023	—	—	—
13	Stolberg Eschweiler (double refined) . . . . .	"	0.0383	0.0050	0.0024	0.0018	0.0025	trace	—	—
14	Herbst and Co. in the Eifel . . . . .	"	0.007	0.003	0.005	0.003	0.0006	—	trace	—
15	Herbst and Co. " " . . . . .	1869	0.0051	0.0045	0.002	—	—	—	0.001	—
16	Prath and Jung . . . . .	"	0.00268	0.00924	0.00121	—	0.00275	—	—	0.00083
17	Stolberg, Eschweiler Gesellsch. . . . .	1867	0.0501	0.0021	0.0008	—	0.0044	0.002	—	—
18	Mechnich . . . . .	1869	0.00243	0.00188	0.0009	—	—	—	0.00075	—
19	Real Compania Asturiana de minas Rentana, } refinado R.C.A. superior . . . . .	1868	0.00057	0.00133	0.00124	0.00008	0.0004	0.01041	trace	—
20	Falé and Co. in Brabant . . . . .	1869	0.00553	0.00190	0.02639	0.00129	trace	0.00385	—	—
21	Stolberg, Eschweiler Gesellschaft . . . . .	1870	0.001872	0.002485	0.00064	—	0.001005	0.003655	0.000922	—
22	Refined Harz Lead from Lautenthal . . . . .	"	0.001413	0.005698	0.002289	0.000834	0.00046	0.005487	0.00088	—
23	" " " Altenau . . . . .	"	0.002022	0.003335	0.001229	0.000776	0.000721	0.003650	0.000707	—

The dioxide acts on heated phosphorus trichloride with ignition, according to the equation:



(Michaelis, *J. pr. Chem.* [2], iv. 449).

**Red Lead.**—The usual process of manufacturing red lead by exposing massicot in trays in the same furnace that serves for the production of the massicot is tedious, and often gives an extremely small yield. G. Mercier (*Ann. Ch. Pharm.* clx. 252) observes that this inadequate result is due to the changes of temperature to which, in such a furnace, it is necessarily exposed. The principal point to be attended to, next to access of sufficient air, is constancy of the right temperature: for the temperature at which massicot takes up oxygen, and that at which red lead loses it, lie very near each other. The most favourable temperature for the formation of red lead approaches that of a dull red heat, without, however, reaching it.

The greatest beauty in the red lead corresponds with the greatest increase in weight in the massicot: this is about 2 p.c. But after the maximum weight is reached, the brilliancy of the red lead can still increase or diminish through a change in its molecular condition.

Mercier has constructed a furnace for use on the large scale, best adapted for the manufacture of red lead. It is essentially a large muffle, round which the fire plays in a great number of small channels. By means of easily worked dampers in certain of these channels, the heat can be regulated at pleasure in that part of the furnace. By this furnace in full action and continuously worked, about 4 tons of red lead may be produced in 24 hours.

**LEADHILLITE.** This sulphato-carbonate of lead,  $\text{PbSO}_4 \cdot 3\text{PbCO}_3$ , originally found at Lanark in Scotland, appears from the observations of E. Bertrand (*Bull. Soc. Chim.* [2], xix. 17) to occur also at Iglesias in Sardinia. Some fragments of a mineral from this locality exhibit in polarised light, coloured rings which show that the mineral belongs to the trimetric system; the optic axes are more divergent for the red than for the blue rays. The apparent inclination of the axes in air is about  $20^\circ 30'$  for natural light. The crystals are negative, the acute bisectrix coinciding with the axis of greater elasticity. All the Sardinian specimens exhibit a twin-formation of about  $120^\circ$ , like those from Leadhills. The hardness of the Sardinian mineral is between 2 and 3, rather nearer to 3; that of the Scotch mineral is 2.5. The density of the Sardinian mineral is 6.60 at  $14^\circ$ , which is rather higher than that of the Scotch variety, viz. 6.3 to 6.5, the difference being apparently due to alteration in the former, inasmuch as some parts of the Sardinian crystals are more or less opaque, contain water, and decrepitate when heated, whereas the perfectly transparent portions—which were selected for analysis—contain no water and do not decrepitate.

Another sulphato-carbonate of lead from Iglesias, described by Laspeyres under the name of maxite, is regarded by Bertrand as identical with leadhillite; but, according to Laspeyres, the two species are distinct (see MAXITE).

**LEGUMIN.** See PROTEIDS.

**LEMON-OIL.** See OILS VOLATILE.

**LEMON-TREE.** Analyses of the fruit and leaves of the lemon grown in Sicily have been made by A. Cossa (*Gazzetta chimica italiana*, ii. 365). The results are given in the following table:

	Leaves	Rind	Parenchyma	Seeds	Juice
Potash . . . . .	10.15	34.42	12.99	41.89	54.66
Soda . . . . .	1.78	2.07	1.50	1.88	1.42
Lime . . . . .	61.83	38.87	43.98	16.75	15.19
Magnesia . . . . .	11.06	11.33	11.78	4.62	4.65
Sulphuric anhydride . . . . .	4.85	3.44	3.60	3.39	4.94
Phosphoric anhydride . . . . .	4.67	8.88	22.26	20.18	15.63
Silica . . . . .	3.40	0.66	1.60	1.13	1.77
Undetermined matter and loss	2.17	0.83	2.20	1.26	1.64
	100	100	100	100	100
Ash in 100 parts of dry substance . . . . .	12.86	6.982	2.130	2.821	

The leaves in the natural state contain 56·61 p.c. water, 38·08 organic, and 5·36 mineral substance; the juice contains 86·22 p.c. water, 12·32 organic, and 1·46 mineral substance. A lemon weighs on the average 75·3 grams, and contains in 100 parts, 15·66 rind, 4·51 parenchyma, 1·06 seeds, and 78·77 juice.

The amount of potash in the ashes of the rind, seeds, and juice of the fruit, is large, viz. 41·89 p.c.; as likewise is the percentage of phosphoric anhydride in the ashes of the parenchyma and seeds.

**LEPIDENE**,  $C^{10}H^{16}O$  (see 1st Suppl. 780). *Orylepidene*,  $C^{10}H^{16}O^2$ , which is readily formed by treating a solution of lepidene in acetic acid with nitric acid or chromic acid, is easily further acted upon by chromic acid, *dioxylepidene*,  $C^{10}H^{16}O^3$ , being formed, which crystallises from alcohol in large rhombic, nearly quadratic plates. By the further action of chromic acid, dioxylepidene yields benzoic acid and benzil, but reducing agents do not act upon it. When treated with a weak alcoholic solution of potash, it yields benzoic acid and deoxybenzoin, from which it appears that its rational formula is  $C^{11}H^{16}(C^7H^5O)^2O$  (Zinin, *Zeitschr. f. Chem.* vii. 483).

**LERP-MANNA** (Flückiger, *Arch. Pharm.* [2], cxlvi. 543). This substance occurs on the leaves of *Eucalyptus dumosa*, and consists of white threads clotted together by a syrup proceeding from the insect (*Psylla Eucalypti*) which spins those threads. It contains, in round numbers, of water 14 parts, threadlike portion 33 parts, sugar 53 parts. The threads possess many of the most characteristic properties of starch, from which, however, they are sharply distinguished by their form. When lerp is washed with water, the sugar dissolves and the threads swell but slightly, but dissolve to a slight extent, so that the solution is coloured blue by iodine. The threads freed from sugar by washing consist of a substance called *Lerp-amylum*.

Lerp-amylum is very slightly soluble in cold water, not perceptibly more so in water at 100°, but entirely soluble to a thin transparent liquid when heated to 135° in sealed tubes with 30 parts of water; this solution on cooling deposits the original substance in flocks, without forming a jelly at any time. The separation is almost complete.

If the material employed in this experiment were originally free from sugar, the liquid left after the separation of the flocks will also be free from sugar. The flocks deposited from solution are insoluble in boiling water; therefore lerp-amylum suffers no chemical change on being heated to 150° with water. Heated in the air-bath to 190° while dry, it turns brown, and is afterwards merely reddened by solutions of iodine; at the same time it becomes partly soluble in hot water: hence it appears that lerp-amylum undergoes a change similar to that which occurs when starch is converted into dextrin. By oxidation with nitric acid, it yields oxalic acid but no mucic acid; it is neutral to vegetable colours, and is not precipitated by lead acetate, and is therefore not to be confounded with the gums, &c.

It gave by analysis 43·7 and 43·07 carbon, 6·6 and 6·4 hydrogen, agreeing with the formula  $C^{11}H^{16}O^4$  (44·4 C and 6·2 H). Like starch, lerp-amylum rotates the plane of polarisation to the right; and on digestion with dilute sulphuric acid, &c., forms a crystallisable carbo-hydrate which agrees in its properties with dextrin. It is insoluble in ammonia cuprate, and is homogeneous.

Though the behaviour of lerp-amylum to iodine and to water, and its insolubility in cuprammonia distinguish it from cellulose, it is to be borne in mind that there are forms or conditions of cellulose which are blued by iodine and dissolve in water.

**LEUCANILINE**,  $C^{10}H^{11}N$ . O. Follenius (*Monit. scient.* [3], i. 678) prepares this base by boiling a solution of rosaniline with zinc-powder till it is completely decolorised. The filtered solution, on cooling, deposits crystals of leucaniline, which may be purified by solution in alcohol, and precipitation with water. Colourless leucaniline, digested in acetic acid, immediately yields a red solution (? from formation of rosanilino), which, on evaporation, gives off acetic acid and leaves a brown mass, turning green when moistened with hydrochloric acid, and then dissolving in water with red colour.

*Leucaniline oxalate* is obtained on mixing the alcoholic solutions of aniline and oxalic acid, in the form of a precipitate which dissolves sparingly in cold, easily in warm water, but crystallises with difficulty and turns red after a while. By dry distillation it yields an oil which is soluble in water and has an odour recalling those of crocote and bitter-almond oil.

**LEUCAURIN**. See AURIN (p. 119).

**LEUCINE,  $C^6H^{11}NO^2$ .** *Amidocaproic Acid.*—G. Hüfner (*J. pr. Chem.* [2], i. 6) has compared natural leucine (prepared from horn-shavings by sulphuric acid, or from fibrin by pancreatic digestion) with leucine prepared by his own process from fermentation caproic acid (heating the bromocaproic acid obtained therefrom with aqueous ammonia, 1st *Suppl.* 782), and with that prepared from valeral-ammonia. The two former appeared, as regards their solubility in water (3.7 to 3.9 p.c. at  $20^\circ$ ), and their subliming point ( $170^\circ$ ) perfectly identical, whereas the leucine obtained by the third process dissolved at  $12^\circ$  in 117.5 parts water (leucine from caproic acid under similar conditions required for solution only 48.8 parts). With regard, however, to their copper-compounds and their nitrates, and to their reaction with manganese peroxide and sulphuric acid, the three leucines were found to be perfectly similar. On the ground of these observations Hüfner regards their identity as established.

The preparation of leucine from valeral-ammonia by the action of hydrocyanic and hydrochloric acids is not easy. The valeral-ammonia must be quite pure and crystalline, and all excess of hydrocyanic acid must be avoided. Hüfner first prepares the compound  $C^6H^{11}N^2.HCl$ , obtained by Strecker and by Köllner (1st *Suppl.* 782) and decomposes it by boiling with hydrochloric acid. To prepare the hydrochloride just mentioned, it is sufficient to dissolve 2 parts of valeral-ammonia in 1 part of aqueous hydrocyanic acid, leave the solution for a night at the temperature of the room, and then mix it with excess of hydrochloric acid.

*Leucine from Vegetable Proteids.*—Ritthausen a. Kreuzler (*J. pr. Chem.* [2], iii. 307; *Chem. Soc. J.* [2], ix. 719), have examined the leucine obtained by boiling these proteids with dilute sulphuric acid, or as a by-product in the preparation of aspartic and glutamic acids. When separated from the other products of the reaction, it is always very impure. For purification it was exhausted with boiling spirit of sp. gr. 0.89 to 0.90, frequently recrystallised from that liquid, then dissolved in boiling water, with addition of as much barium carbonate as the liquid would take up, and recrystallised from water till the quantity of barium salts remaining in the liquid had become quite inappreciable. After decoloration by animal charcoal, it formed thin shining laminae. But even in this state, it still retained a little sulphur, which could be removed only by boiling with potash and lead oxide.

As all the vegetable proteids examined by Ritthausen a. Kreuzler yielded leucine, it may be assumed that all these bodies occurring in plants are capable of furnishing it. The quantity produced varies, however, according to the particular proteid employed, gluten-proteids and conglutin yielding considerably less than legumin. The quantity of purified leucine obtained varied from 4 to 12 p.c.

Leucine when heated with *soda-lime* does not give off all its nitrogen as ammonia, unless it has been previously mixed with sugar; the same was found to be the case with the copper-compound of leucine.

According to Gössmann and others, an aqueous solution of leucine is not precipitated by *mercurio nitrate*, whereas, according to R. Hoffmann, it gives a white flocculent precipitate (iii. 582). Ritthausen a. Kreuzler find that this precipitation occurs only with impure leucine still retaining aspartic or glutamic acid.

*Copper-compounds.*—Gössmann (*loc. cit.*) by evaporating the blue solution produced by boiling leucine with cupric oxide obtained the compound  $2C^6H^{11}NO^2.CuO$  in crystalline grains. Ritthausen a. Kreuzler, by boiling a very dilute solution of leucine with cupric hydrate, obtained the compound  $3C^6H^{11}NO^2.2CuO$  in light violet-brown scales, sparingly soluble in water. The light blue compound which Köhler obtained by boiling leucine with cupric acetate (1st *Suppl.* 782) has, according to Ritthausen a. Kreuzler, the composition  $7C^6H^{11}NO^2.4CuO$ .

**LEUCINITRIL,  $C^6H^{11}NO = C^6H^{12}O^3$**  (leucic acid) +  $NH^3 - 2H^2O$ . This body, also called *leucimide*, is related to leucic acid in the same manner as acetonitril to acetic acid. It was first obtained by Köhler by dehydration of leucine (1st *Suppl.* 782), and has been more particularly examined by Thudichum (*Chem. Soc. J.* [2], viii. 409), who prepared it by Köhler's method; also from the decomposition-products obtained by the action of sulphuric acid on proteids. These products, after evaporation, were left for some time in contact with the air, and then treated for several weeks with ether or alcohol. These solutions, when left to evaporate, yielded the nitril, which was purified by crystallisation from hot alcohol, and decoloration with animal charcoal. The product thus obtained is, however, very small, and Thudichum, therefore, gives the preference to Köhler's method.

Leucinitril forms white, faintly lustrous, microscopic, rhombic needles which easily melt and sublime. It is insoluble in cold, slightly soluble in boiling water, soluble

also in alcohol, more easily in hot alcohol, less soluble in ether. Concentrated aqueous ammonia and potash have no action upon it, even at the boiling heat; hot hydrochloric acid dissolves a trace; it dissolves in strong acetic or nitric acid, and separates unaltered on addition of alkali or on evaporation. An alcoholic solution of leucinitril mixed with tincture of iodine gives off a small quantity of hydriodic acid, and on addition of potash and a large quantity of water, deposits white crystals.

In the preparation of leucinitril by Thudichum's method, there is often obtained, as secondary product, a substance rich in sulphur, which forms nacreous crystalline laminae more soluble in ether than leucinitril, and giving off hydrogen sulphide when boiled with a solution of lead oxide in potash. Thudichum names this substance *thioterin*. It is not formed when an ethereal or alcoholic solution of leucinitril is treated with hydrogen sulphide.

**LEUCITE.** Out-casts of Leucite from Vesuvius have been described by G. vom Rath (*Pogg. Ann.* cxlvii. 263). This mineral, the most important and characteristic of all those which occur on Vesuvius and in its lavas, occupies to a certain extent an exceptional place among minerals. It exhibits no varieties, and there are no species isomorphous with it. Of all rock-forming minerals it is the most limited in the mode of its occurrence. Felspar, which, in a chemical point of view, is most nearly allied to leucite, occurs in rocks of all ages, and in beds of every species, but leucite is never found in veins, very rarely in druses of lava or of ejected masses, never in pseudomorphs. Its occurrence in lava might perhaps seem to remove all doubt as to its mode of formation and its crystallisation from a fused mass. Nevertheless the various minerals which constitute lava cannot all have separated from the mass during solidification. It is possible, and even probable, that leucite may have crystallised from lava, but the crystallisation must have taken place, not during the flow of solidification of the lava on the surface, but in the unknown depths below. On Somma, leucite not only forms the lavas, but likewise appears in out-casts, sometimes in limestone blocks, sometimes in sanidine aggregates. The following are descriptions of some remarkable specimens of both these classes of leucitic out-casts.

(a.) A lump of limestone about 10 cm. thick, interspersed with grains of calcspar and very small octohedrons of spinelle and periclase, containing moreover numerous roundish cavities from 3 mm. to 3 cm. in diameter, in which occur rounded grains of leucite, some firmly fixed in the cavities, others loose, so that they rattle when the stone is shaken. The leucite in the interior of these grains has the ordinary constitution, and is intergrown with black augite; externally they are covered with a white very prickly crust, consisting of silky, fibrous prisms 1 mm. long, firmly attached to the grains and arranged in nearly parallel rows. This white mineral, when freed by acetic acid from calcium carbonate (amounting to 15–18 p.c. of the whole), gives by analysis 41.1 p.c. silica, 34.5 alumina, 5.6 lime, 0.7 magnesia, and 18.1 loss (alkalis), whence it appears to be *davyne*.

The calcareous matrix consists of 60.7 p.c. soluble and 39.3 insoluble in acetic acid. The soluble portion is a magnesian limestone containing 86.5 p.c.  $\text{CaCO}_3$  and 13.5  $\text{MgCO}_3$ , therefore not a true dolomite. A similar composition was found by Marchand in a fine-grained block of limestone from the Fosso di Pollena.

The insoluble portion of the calcareous matrix appears under the microscope perfectly crystalline, and as a mixture of colourless grains, probably quartz-sand, greenish octohedrons of periclase, black octohedrons of ceilanite, and a very small quantity of magnetic iron ore. It gave by analysis 0.5 p.c.  $\text{FeO}^*$ , 38.6  $\text{SiO}_2$ , 10.7  $\text{Al}_2\text{O}_3$ , 43.1  $\text{MgO}$ , 8.3  $\text{FeO}$  (=101.2). The alumina may be regarded as combined with the magnesia and ferrous oxide, forming ceilanite; the excess of magnesia with the rest of the ferrous oxide forms periclase, while the silica is probably present in the free state. Not a trace of lime was found in the insoluble portion of the matrix.

(b.) A stone 12 centimeters thick, having the form of a segment, apparently about one-fourth of the original spheroidal block. It consists of a calcareous shell 3 to 4 cm. thick, surrounding a pear-shaped nucleus of leucite of granular structure and abundantly traversed by black augite. In the interior is a cavity lined with fine crystals of leucite and augite. At the boundary between the shell and the nucleus are numerous shining dodecahedrons of reddish-brown garnet, 1–1½ mm. in size, partly imbedded in the leucite mass, which separates easily and smoothly from the calcareous shell, partly resting on the inner side of the latter. The leucite nucleus is immediately surrounded by a radio-fibrous zone 1–1½ cm. broad, the fibres having a light greenish-grey colour. This fibrous mineral, freed by treatment with acetic acid from intermixed calcium carbonate, gave by analysis 38.6 p.c.  $\text{SiO}_2$ , 18.4  $\text{Al}_2\text{O}_3$ , 4.2  $\text{FeO}$ , 2.8  $\text{CaO}$ , 24.7  $\text{MgO}$ , and 11.3 loss (alkalis); showing that it consists of biotite or magnesia mica. This and the garnet have probably been formed from the leucite and the limestone where they

were in contact, under the influence of a very high temperature, the existence of which is shown by the marks of fusion at the boundary between the shell and the nucleus. To account for the occurrence of leucite in a shell of limestone is by no means easy, for the latter cannot be regarded as the true matrix of the leucite. The leucite nuclei of this and the preceding out-cast must rather be regarded as foreign enclosures in the limestone; but it is difficult to see how the limestone can have enclosed the leucites like a plastic mass.

(c.) A sanidine stone, containing very numerous crystals of leucite, 5 to 28 mm. in size. The matrix consists of a fine-grained mixture of predominant sanidine, black hornblende, brown garnet, and a small quantity of magnetic iron oxide, also separate tabular crystals of sanidine measuring 20 mm. The leucites are white, with conchoidal fracture, very fresh, some unusually pure, others showing admixtures of hornblende. They are not sharp-edged, but rather rounded, and are surrounded with a crust 1-1½ mm. thick of small, beautifully formed crystals of sanidine. These appearances might seem to indicate the commencement of a pseudomorphosis of sanidine after leucite, a change which Rammelsberg observed in its completeness in an out-cast very similar to the one under consideration. Closer observation shows, however, that this can hardly be the case. On breaking a leucite nodule from the stone, the sanidine envelope remains behind in the form of a druse lined with the most beautiful crystals of sanidine, firmly attached to the ground-mass, and consisting indeed of purer crystals growing out of it. The separated nodule of leucite is also covered with slender crystals of sanidine firmly implanted on it, and the surface of the leucite itself is developed into innumerable small but well-defined crystals, arranged in parallel rows. Now, when one mineral has been formed from another, or when the process of transformation is in progress, one of the minerals is sure to be found in parts presenting the appearance of the other, and intermediate stages of this transformation are likewise met with. In the present case, however, the closest examination with the microscope shows nothing of the kind. On the contrary, the surface of the leucite nodule is seen to be covered with crystals of leucite and sanidine placed side by side, and both in perfect freshness. Moreover, the stone is perfectly closed, no crack or channel being visible in which alteration of composition might be expected to occur.

For these reasons vom Rath thinks it more probable that when the large rounded crystals began to form, their chemical composition was somewhat different from the typical composition of leucite; perhaps the following: 55.96 p.c.  $\text{SiO}_2$ , 23.0  $\text{Al}_2\text{O}_3$ , 21.04  $\text{K}_2\text{O}$ , which is that of a mixture of  $\frac{1}{3}$  sanidine and  $\frac{2}{3}$  leucite, and that this mixture afterwards split up into the two minerals, which, indeed, occur on the leucite nodules in about this proportion. The leucite, so remarkably distinguished by its shell of sanidine, exhibits nearly the normal composition:

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$
Analysis . . .	55.58	23.38	0.26	19.53	1.60 = 100.25
Calculation					
$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ }	55.0	23.5	—	21.6	— = 100

Leucite has been found in microscopic unaltered crystals in the tufas of the Schlossberg of Ackharrn in the Kaiserstuhl range (F. Sandberger, *Jahrbuch f. Mineralogie*, 1870, 207).

In leucite from Andernach, J. L. Smith (*Sill. Am. J.* [2], xlix. 335) found 54.75 p.c.  $\text{SiO}_2$ , 23.03  $\text{Al}_2\text{O}_3$ , 1.55  $\text{Fe}_2\text{O}_3$ , and 20.06 alkali, reckoned as potash. The quantities of alkali in other leucites were found to be: from Vesuvius, 21.85; from Berghetta, 20.69; from Frascati, 20.38, exclusive of undetermined quantities (up to 0.9 p.c.) of rubidia and caesia.

**Crystalline System of Leucite.** This mineral has hitherto been regarded as belonging to the monometric system and having the form of the icosi-tetrahedron (ii.125); but G. vom Rath (*Jahrb. f. Mineralogie*, 1873, 113), from the examination of the leucite crystals implanted in the druses of the Vesuvian out-casts above described, has come to the conclusion that the mineral really belongs to the dimetric or quadratic system.

The faces of these implanted crystals are characterised by a peculiar striation, the lines running parallel either to the shorter (so-called hexahedral) edges, or to the symmetric diagonals of the trapezoidal faces. These lines often begin in the middle of a face and are not continued to an edge; but when one of them reaches an edge, it does not usually stop there, but is prolonged into the adjoining face; the line and its prolongation being situated in a plane, which, assuming the form of leucite to be the regular icositetrahedron, is parallel to the truncation-face of the symmetrical summit of



the crystal, or, in other words, to the face of a rhombic dodecahedron. Thus, for example, in the right upper octant (fig. 19) the principal striae lie in the dodecahedral face which truncates the left upper symmetric summit. The plane of the striae which run over  $i^2$  in the diagonal direction, over  $o^2$  and  $i^4$ , parallel to the combination-edge of this latter face, corresponds with the truncation-face of the right upper symmetric summit. The two long striae which, running over the combination-edge  $i^4 : i^2$ , have a similar position on the two faces, viz. parallel to the edges  $i^2 : o^2$  and  $i^2 : o^4$ , correspond with the dodecahedral face which truncates the front upper symmetric summit. The shorter groups of lines on  $i^2$  and  $i^4$  (parallel to the edges  $o^1 : i^2$  and  $o^2 : i^4$ ) are similarly situated with regard to the back upper summit. In like manner it is possible to determine the dodecahedral face in which every stria passing over an edge is situated.

On viewing the crystals by lamplight, it is easily seen that the striation is not merely superficial, but is due to interposed twin-lamellae. Sometimes indeed the striae have a very perceptible breadth, and their surface shines in a position different from that in which the general face of the crystal appears lustrous, the bands remaining dark while the general surface is bright, and *vice versa*. If, for example, the face  $o^1$  be viewed in such a position that it shines, the striae are then dark; but on turning the crystal for about  $5^\circ$  round an axis parallel to these striae, i.e. to the edge  $o^1 : i^1$ , the twin-lamellae shine while the face itself becomes dark. In short, the striation of these implanted leucites exhibits the closest possible analogy to that of triclinic feldspar, which is known to arise from the interposition of twin-lamellae.

Fig. 19.

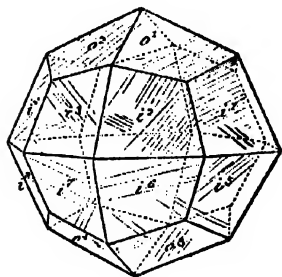
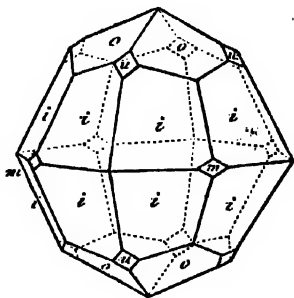


Fig. 20.



From the appearances above described, it may be inferred with certainty that these striated leucites do not belong to the regular or monometric system; for in that system a twin-formation parallel to a dodecahedral face cannot occur. If indeed an icositetrahedron be cut parallel to the face of the dodecahedron and turned round  $180^\circ$ , no projecting or re-entering angles will be formed, but the whole will return into its former position.

The conclusion thus deduced is confirmed by exact measurements of the angles of the leucite crystals, from which it appears that edges which ought to be identical if the crystals were monometric, really differ by about 4 degrees.

Leucite belongs in fact to the quadric or dimetric system, its form, hitherto regarded as a regular icositetrahedron, or leucitohedron, being a combination of a quadric octohedron with a di-octohedron (fig. 20).

Octohedron,  $o = a, a, c$ , or  $P$

Di-octohedron,  $i = \frac{1}{2}a, \frac{1}{2}a, c$ , or  $4P2$ .

These faces exhibit a remarkable equality of development. The following also sometimes occur subordinate:

First acute octohedron,  $u = \frac{1}{2}a, \infty a, c$ , or  $2P\infty$

First quadric prism,  $m = a, a, \infty c$ , or  $\infty P$ .

The ratio of the lateral axes to the vertical axis, deduced from the measurement of the lateral edge of the di-octohedron, is—

$$a : c = 1.8988 : 1 \text{ or } 1 : 0.05637.$$

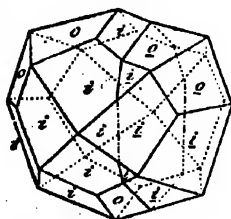
The following are the principal angles:—

Terminal edge of the octohedron . . . . .	= $130^{\circ} 3'$
Lateral edge of the octohedron . . . . .	= $73^{\circ} 19' 40''$
Primary terminal edge of the di-octohedron (situated under the octohedral edge) . . . . .	= $131^{\circ} 23'$
Secondary terminal edge (situated under the octohedral face) . . . . .	= $148^{\circ} 9' 30''$
Basal angle of the di-octohedron (situated at the ends of the lateral axes) . . . . .	= $126^{\circ} 52' 15''$
Basal angle of the di-octohedron (situated between the lateral axes) . . . . .	= $143^{\circ} 7' 35''$

The plane angles of this base are the same as those of the three sections through the octohedral edges of the icositetrahedron 202.

The law of twin-formation of leucite is that 'The twin-plane is a face of the first acute octohedron;' and by this plane the crystals are united. The twin-plane is inclined to the vertical axes at an angle of  $43^{\circ} 31'$ ; to one of the lateral axes at  $46^{\circ} 28' 15''$ . Leucite, hitherto supposed to be incapable of forming twins, is in reality very much inclined to twin-formation, exhibiting very regular combinations of two or more individual crystals, and also polysynthetic crystals in which, as above described, the principal crystal is intersected by laminae parallel to the faces of the first acute octohedron.

FIG. 21.



The simplest of these twin-formations is represented in fig. 21.

Imbedded leucites do not admit of exact angular measurement, but they frequently have obtuse projecting and re-entering angles, and exhibit the polysynthetic structure in a very high degree. There can, therefore, be little doubt that they are also quadratic, like the implanted crystals.

The chemical analysis of leucite crystals from the same druse as those whose angular measurement has been above given, exhibits the following composition—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	CuO	K <sup>a</sup> O	Na <sup>a</sup> O
55.21	23.70	0.43	10.83	1.21 = 100.38

agreeing almost exactly with the leucite formula,  $K^aO \cdot Al^aO^a \cdot 4SiO^a$ , which requires 54.92 SiO, 23.52 Al<sup>a</sup>O<sup>a</sup>, and 21.56 K<sup>a</sup>O. The proportion of soda in these striated crystals is not greater than in crystals of leucite previously examined, and regarded as monometric (Rammelsberg found 6.43 p.c. Na<sup>a</sup>O in a Vesuvian leucite): consequently the quadratic form cannot be regarded as a peculiarity of these crystals, due to the presence of soda.

The optical characters of leucite are more in accordance with the quadratic than with the hitherto assumed monometric form. Des Cloizeaux (*Nouvelles recherches sur les propriétés optiques des cristaux*, 1867, pp. 3-5) observes that leucite, when examined by polarised light, does not behave like a monometric crystal, the appearances varying according to the particular plate examined, and the direction in which it has been cut from the crystal. He also remarks that the striae seen in polarised light are parallel to the planes of a dodecahedron. These striae, due to interposed twin-lamellae, had been previously observed by Biot, who founded upon them his theory of lamellar polarisation.

Leucite may therefore take its place amongst the series of quadratic minerals which are so characteristic of Vesuvius, viz., zircon, humboldtilite, meyonite, mizsonite, sarcophile and vesuvian, to the last of which it approximates very closely. The primary form of vesuvian has, according to v. Zepharovich, an angle of  $129^{\circ} 20'$  in its lateral edge, and amongst its numerous combinations there occurs the di-octohedron 4P2, which is otherwise not frequently observed. If the primary form of vesuvian were associated with this di-octohedron, a form would be produced almost exactly like the regular icositetrahedron, as in the case of leucite (vom Rath).

**LEUCOLINE.** Ballo (*Dingl. polyt. J.* cii. 377) has obtained from crude naphthalene an oily liquid containing leucoline. A quantity of the crude naphthalene, which had never been treated with acids or alkalis, was boiled on the water-bath, and the brown solution obtained was precipitated with ammonia. A specimen precipitate was formed, which on drying at a higher temperature or in a vacuum over sulphuric acid, always fused to a dark thick fluid, possessing in an eminent degree the characteristic odour of impure naphthalene. Potassium bichromate produced a bulky precipi-

tates, which dried up to brown hard masses, but the precipitation was not complete. The oily liquid obtained as above was distilled, a light brownish-yellow coloured distillate coming over; it was then further purified by fractional distillation, the portion coming over at  $240^{\circ}$  being collected. The distillate was not fully soluble in hydrochloric acid. By shaking with dilute hydrochloric acid, pouring off from the indifferent oils, and then adding ammonia to the solution, the oily body was precipitated in a milky form, gradually collecting in drops at the bottom of the vessel. This oily layer was completely soluble in hydrochloric acid. Dried in a vacuum, it was quite clear, but became somewhat dark-coloured. To this body Ballo gives the name of *leucoline oil*. It appeared to be a mixture of several bases, but did not yield any precipitate of constant composition by fractional precipitation with ammonia; neither did it form any crystalline salts. The sulphate is precipitated from the ethereal solution of the oil, after addition of a few drops of dilute sulphuric acid, in the form of a yellowish-brown oil, and in the strongly acid aqueous solution of the sulphate, potassium bichromate produces a bulky yellow precipitate. Red litmus paper is not turned blue by the oil; it produces grease stains on blotting paper. These properties render it probable that the oil contains leucoline. Platinic chloride yields in a solution of leucoline oil in dilute hydrochloric acid a yellow precipitate; and in the filtrate, after standing some days, further portions crystallise out in long feathery groups of orange-yellow needles. These dried in a vacuum over sulphuric acid, and then at  $100^{\circ}$ , gave by analysis 28.03 p.c. platinum, agreeing nearly with the platinichloride of lepidine  $2(C^{10}H^9N.HCl).PtCl^4$ , which requires 28.3 p.c. platinum. The first formed precipitate was only partially soluble in alcohol; the undissolved portion contained 29.2 p.c. and the recrystallised portion 29.7 p.c. platinum. The formula of leucoline platinio-chloride,  $2(C^{10}H^9N.HCl).PtCl^4$ , requires 29.3 p.c. platinum.

Leucoline oil appears therefore to be a mixture of leucoline and lepidine. Treated with amyl iodide and potash-ley, it gives a violet colouring matter, apparently identical with that obtained from cinchonine-chinoline (i. 873; 1st Suppl. 431).

This last result appears to contradict the statement of C. Groville Williams that coal-tar leucoline gives no colour when treated with amyl iodide and potash. Williams, however (*Chem. Soc. J.* [2], x. 657), has repeated his former experiments with the same result as before, viz., that chinoline gives at once and without difficulty a brilliant and characteristic blue colour, whereas leucoline gives only a faint, dirty, purplish coloration, having no resemblance whatever to chinoline-blue. He therefore infers that coal-tar sometimes contains chinoline as well as leucoline, a conclusion which is strengthened by the fact that so-called leucoline from coal-tar has been found by Hofmann to give with chromic acid the yellow crystalline precipitate characteristic of chinoline, whereas Williams's experiments show that perfectly pure leucoline gives only a yellow oily precipitate.

**LEUCOPHANE.** This mineral (iii. 584) is trimetric, and according to v. Lang (*Jahrbuch für Mineralogie*, 1872, 426) has the axial ratio.  $a : b : c = 0.9657 : 1 : 0.697$ . The tabular crystal examined exhibited the faces  $OP$ ,  $\infty P$ ,  $2P_{\infty}$ ,  $\frac{1}{2}P_{\infty}$ ,  $P$ ,  $2P$ ,  $P_2$ ,  $P_2$ . Cleavage parallel to  $OP$ .

**LEUCOROSOLIC ACID.** See ROSOLIC ACID.

**LEVULOSE.** See SUGARS.

**LICHENS.** According to W. Knop (*Chem. Centr.* 1872, 172), the ashes of lichens contain alumina. He considers this substance to be dissolved out of the dust which settles on the lichen and firmly adheres to its surface after wet weather, by the oxalic acid which is known to be a frequent constituent of lichens, this acid being one of the best solvents of alumina. He also thinks it probable that the oxalic acid in lichens is produced during the growth of the plant from what he names the 'lichen acids;' for treatment of these acids with caustic alkalis produces a carbonate or an oxalate.

Referring to the researches of Schwendener, from which lichens appear to be, not distinct plants, but combinations of fungi with algae, the gonidia of the lichen consisting of algae that have become enclosed in the hyphae (mycelium) of a fungus which then grows into the thallus of the lichen, Knop points out that the lichen-acids are found exclusively in the cortical layers of the lichen, that is, in the fungus, and not in the alga (gonidium).

Respecting the nutrition of the two elements of a lichen, he considers that, on the one hand, the alga (gonidium) which in many lichens is completely enclosed within the fungus, obtains its nutrient matters through the fungus, by which they are absorbed in damp weather from the barks of trees or the stones on which the lichen grows, and on the other, that the fungus, which cannot be converted into a lichen without the presence of an alga, and cannot of itself fix carbonic anhydride, has its food elaborated for it by the alga.

Lastly, he suggests that the detection of a particular lichen-acid in the *soridia* of lichens may aid in determining the lichen to which they belong.

**LIGHT. Refraction and Dispersion.**—Gladstone (*Chem. Soc. J.* [2], viii, 101, 147) has collected together the results published in his previous papers on the subject (see iii, 624-631, and 1st *Suppl.* 783-785), and shown, with respect to a large number of hydrocarbons, that the values of the refraction-equivalents calculated according to the method already described agree very closely with those determined by observation. Exceptions to this agreement are, however, exhibited by the hydrocarbons of the aromatic group, by two series of nitrogenised bases, viz., the pyridine and chinoline series, and by certain oxidised essential oils, whose observed refraction-equivalents are considerably higher than those calculated from the values of the elements (1st *Suppl.* 785). Gladstone is inclined to attribute this deviation to the circumstance that the phenylic nucleus  $C^6H^5$  exerts as a whole upon the rays of light a predominating influence, which is not destroyed when the hydrogen in the nucleus is replaced by chlorine, nitric oxide, oxygen, and sulphur. The deviations from the normal refraction-equivalent exhibit a regularity depending on the composition, which for the typical hydrocarbons may be represented as follows:—

Hydrocarbons	Typical formula	Refraction-equivalent
Paraffins . . . . .	$C^nH^{2n+2}$	Normal
Olefines . . . . .	$C^nH^{2n}$	"
Terpenes . . . . .	$C^nH^{2n-4}$	" + 3
Benzene and its homologues . . . . .	$C^nH^{2n-6}$	" + 6
Naphthalene . . . . .	$C^nH^{2n-12}$	" + 14
Anthracene . . . . .	$C^nH^{2n-18}$	" + 17

Similar relations are exhibited by a series of oxidised compounds which differ from one another only in their amount of hydrogen:—

Substance	Formula	Refraction-equivalent
Peppermint Camphor . . . . .	$C^{10}H^{20}O$	Normal
Dihydrate of Cajeput . . . . .	$C^{14}H^{28}O$	"
Wormwood oil . . . . .	$C^{14}H^{28}O$	" + 1
Carvol . . . . .	$C^{14}H^{28}O$	" + 6
Anethol . . . . .	$C^{14}H^{28}O$	" + 13

The first of the two following tables gives the refractive indices, for the lines A, D, H, of a number of compounds not previously examined, whose refraction-equivalents have the normal values. The second gives the refractive indices of several compounds whose observed refractive-equivalent is greater than that determined by calculation.

TABLE I.—Normal Refractive Indices.

Substance	Equivalents of Solvent	Specific Gravity	Temp. Centigrade	Refractive Indices		
				A	D	H
Hydrate of turpentine-oil . . . . .	63.58 alcohol	0.819	9	1.3690	1.3752	1.3846
Camphor . . . . .	4.54 "	0.866	8.5	1.4023	1.4067	1.4208
Dihydrate of Cajeput . . . . .	—	0.916	20	1.4532	1.4588	1.4745
Oil of wormwood . . . . .	—	0.927	20	1.4543	1.4588	1.4786
Sugar . . . . .	9.10 water	1.340	7	1.4588	1.4687	1.4771
Potassium succinate . . . . .	71.50 water + 0.28 $C^{12}H^{24}O_4$	1.093	9	1.3617	1.3669	1.3679
Urea . . . . .	7.00 water	1.088	28.5	1.3703	1.3819	1.3952
Acetyl chloride . . . . .	—	1.169	—	1.3992	1.4042	1.4218
Chloroform . . . . .	—	1.478	9	1.4616	1.4679	1.4876
Camphene hydrochloride . . . . .	39.92 alcohol	0.823	9	1.3713	1.3767	1.3876
Iodoform . . . . .	38.64 ether	0.820	9	1.3671	1.3716	—
Ammonium sulphocarbonate . . . . .	35.47 water	1.066	—	1.3916	1.3968	—
Ammonium sulphocarbonate . . . . .	18.71 "	1.091	10	1.4171	1.4254	—
Potassium xanthate . . . . .	24.24 "	1.106	4	1.3891	1.3991	—
Potassium chloride . . . . .	126.76 "	1.082	17	1.3334	1.3374	1.3468
Potassium bromate . . . . .	103.49 "	1.085	17	1.4341	1.4399	1.4501
Metaphosphoric acid . . . . .	8.23 "	1.270	20.5	1.3718	1.3764	1.3861
Orthophosphoric acid . . . . .	13.30 "	1.180	7.5	1.3584	1.3639	1.3736

TABLE II.—*Abnormal Refractive Indices.*

Substance	Equivalents of Solvent	Specific Gravity	Temp. Centigrade	Refractive Indices		
				A	D	H
Benzene	—	0.887	11	1.4953	1.5052	1.5393
"	—	0.878	10	1.4925	1.5021	1.5358
"	—	0.886	7	1.4981	1.5077	1.5431
Cymene	—	0.872	11	1.4801	1.4877	1.5130
Nitrobenzene	—	1.193	7	1.5438	1.5565	—
"	—	1.191	8	1.5426	1.5564	—
"	—	1.126	8	1.5244	1.5398	1.5942
Phenyl sulphide	—	1.092	11	1.3687	1.3638	1.3767
Potassium sulphophosphate	111.36 water	0.802	12.5	—	1.3775	—
Chlorhydril	23.74 ether	0.859	7	1.3913	1.3962	1.4116
Benzic acid	11.14 alcohol	0.838	8.5	1.3806	1.3850	1.3993
"	17.44 "	1.139	6	1.8917	1.8974	1.4149
Potassium benzoate	22.90 water + 0.06 K <sup>2</sup> O	1.091	6	1.3705	1.3757	1.3804
"	38.24 water + 0.09 K <sup>2</sup> O	1.228	10	1.5438	1.5568	1.6012
Benzoyl chloride	—	1.059	11	1.6045	1.6253	—
Chloranil hydride	—	0.789	6	1.3950	1.4005	1.4189
Naphthalene	—	0.9877	—	1.5430	—	1.6129
Anethol	7.95 ether	0.832	8	1.3845	1.3890	1.4031
Thymol	18.89 alcohol	0.944	6	1.4868	—	1.5160
Myristic acid	—	0.9107	24	0.4767	1.4802	1.5028
" another specimen b.p. 212-218°						

*Refraction and Dispersion of Selenium.*—This substance exhibits very great refractive and dispersive power. The dispersive power of the rays A to C, that is to say, the magnitude  $\frac{n_c - n_A}{n_A - 1}$  is  $6\frac{1}{2}$  times, and  $n_c - n_A$   $1\frac{1}{2}$  times as great as in carbon bisulphide. The refractive indices of the following Fraunhofer lines have been determined:

$n$	A	a	B	C	c	D
	2.654	2.692	2.730	2.787	2.857	2.78.

The first four numbers are very exact (at least to 5 units of the third decimal place); the last two are less exact, inasmuch as beyond the line D, no more light passes through a film of selenium 0.003 mm. thick (J. L. Sirks, *Pogg. Ann.* cxliii. 429).

For Croullebois' measurements of the Refraction and Dispersion of Gases and Vapours, see *Compt. rend.* lxvii. 692; *Ann. Ch. Phys.* [4], xx. 136; *Jahresb. f. Chem.* 1868. 122; 1870, 170.

For the same physicist's determinations of the refractive power of Water, Methylie, Ethylic, and Amylic Alcohols, Ethylic Ether, Carbon Bisulphide, Turpentine-oil and Lemon-oil, see *Ann. Ch. Phys.* [4], xxii. 139; *Jahresb.* 1871, 153.

*Refraction and Dispersion of Opaque Bodies.*—A method of determining the refractive indices and dispersive powers of bodies which, like metallic oxides and chlorides, are opaque in the mass but transparent in very thin films, has been devised by W. Wernicke (*Pogg. Ann.* cxxxix. 132). Such films may be formed in great perfection on clean plates of the metal by electrolytic action, and their thickness determined by weighing. They exhibit the interference colours of thin plates, and on viewing them through a spectroscope, spectra are seen with well-defined alternate bright and dark bands, from the number and position of which the wave-lengths of the several Fraunhofer lines can be determined. By this method the following results have been obtained:—

Substance	Sp. gr.	Refractive Indices					
		B	O	D	E	F	
Cuprous oxide, Cu <sup>2</sup> O	5.975	2.534	2.558	2.705	2.816	2.963	
Hydrate of Lead dioxide	6.169	1.802	2.010	2.229	—	—	
Hydrate of Manganese dioxide	2.542	—	1.801	1.862	1.944	—	

The refraction and dispersion of cuprous oxide are the greatest hitherto determined with certainty in any substance.

From a series of observations extending to numerous other bodies, Wernicke draws the following general conclusions:—In all bodies of great refractive and dispersive power the absorption increases as the wave-length diminishes, the increase being continuous from a particular part of the spectrum different for each body. In transmitted

light, therefore, these bodies, in layers of sufficient thickness, always appear yellowish-red or red.

The refraction and dispersion of silver chloride, bromide, and iodide have been determined by Wernicke (*Pogg. Ann.* cxliii. 560) in two ways:—

1. By the method above described. A film of metallic silver was deposited on a glass plate by means of ammoniacal solution of silver nitrate mixed with caustic soda and  $\frac{1}{4}$ th of its volume of a reducing liquid prepared by mixing 60 grams of sulphuric acid, 40 alcohol, 35 water, and 50 manganese dioxide; distilling off about 50 c.c. into a vessel containing 60 grams of water; then adding 100 c.c. alcohol, and 10 grams of cane-sugar inverted with nitric acid; and diluting with water to 100 c.c. When the brilliant silver film thus obtained is exposed to iodine-vapour, or when pieces of iodine are laid upon it, the silver is immediately converted into iodide, which exhibits splendid interference colours. To convert the silver speculum into bromide or chloride, the chlorine or bromine-vapour, dry and free from air, must be made to act upon it as quickly as possible, as, if the action goes on long, the transparency of the films is impaired, probably in consequence of the formation of oxychloride or oxybromide.

2. The refraction and dispersion were determined by direct measurement by means of small prisms made by casting the fused salts between plates of parallel glass at the desired angle. Prisms of fused silver iodide exhibited, when cooled to  $138^{\circ}$ , a sudden alteration of colour and transparency, leading to the conclusion that, at high temperatures, part of the iodine is separated from its combination with the silver, and is absorbed by the remaining substance in the liquid state: for the spectrum, like that of solid and liquid iodine, contains no blue or violet light. In the normal state, below  $138^{\circ}$ , silver iodide gives a spectrum less bright but twice as long, and particularly developed in the blue-violet portion.

The following are the results of the observations:—

		Refractive Index for:				
		C	D	F	G	H $\gamma$
Silver chloride	1 method	—	2.071	2.101	2.135	—
	2	2.0462	2.0611	2.0958	—	2.1309
Silver iodide	1	—	2.202	2.267	2.409	—
	2	2.1531	2.1816	2.2787	2.405	—
Silver bromide	1	—	2.261	2.303	2.360	—
	2	2.2331	2.2533	2.3140	—	—

The results obtained by the second method are as exact as those of the first for the iodide of silver, less exact for the chloride and bromide. According to Des Cloizeaux (*Jahresh. f. Chem.* 1867, 44), the refractive index of yellow light for the ordinary ray in a hexagonal crystal of silver iodide = 2.23; in the amorphous iodide, according to Fizeaux (*Compt. rend.* lii. 274) it is 2.246. With regard to the absorption which, in the spectrum of bromide and iodide of silver, begins even between G and H $\gamma$ , and in that of the chloride, behind H $\gamma$ , the three salts follow the law above given. As the temperature rises the refraction of the three bodies diminishes.

*Anomalous Dispersion.*—Leroux showed, in 1862 (*Compt. rend.* lv. 126), that a hollow prism filled with iodine-vapour transmits only a group of red and a group of blue rays, and that the red rays are refracted more strongly than the blue, this effect being quite independent of the particular arrangements and apparatus used. The iodine-vapour likewise transmits the ultra-violet rays. Its dispersive power varies inversely with the temperature. To this previously isolated observation another was added by C. Christiansen (*Pogg. Ann.* cxli. 479), namely, that aniline-red or fuchsine in an alcoholic solution containing 18.8 p.c. of the colouring matter, exhibits very remarkable refraction-phenomena, the indices of refraction for the several Fraunhofer lines being:

B	C	D	F	G	H
1.450	1.502	1.561	1.512	1.285	1.312

increasing from B to a little beyond D, then decreasing rapidly to G, and from that point again increasing.

Christiansen (*Pogg. Ann.* cxliii. 250) further determined the differences between the refractive indices of five Fraunhofer lines and the line H, whose absolute refractive index was also directly measured. The latter measurements are much more uncertain than those of the differences, in which, nevertheless, the errors may amount to four units in the second place of figures. By observation in aqueous solutions of the refracting angles of  $1^{\circ}$  to  $41^{\circ}$ , the following values were obtained for solutions containing 18.8, 17, 8, and 2.5 p.c. fuchsine in alcohol:—

Lines	18.8		17.		8		2.5	
	$n - n_H$	$n$	$n - n_H$	$n$	$n - n_H$	$n$	$n - n_H$	$n$
B.	0.138	1.450	0.118	1.426	—	—	0.011	1.354
C.	0.190	1.502	0.149	1.493	0.084	1.456	—	—
D.	0.240	1.561	0.204	1.548	0.130	1.502	0.046	1.419
E.	0.000	1.312	0.000	1.344	0.000	1.372	0.000	1.373
F.	—0.027	1.285	—0.022	1.322	—0.018	1.354	0.006	1.367
H.	—	1.312	—	1.344	—	1.372	—	1.373

The connection between anomalous dispersion and other optical properties of the bodies which exhibit it was first pointed out by A. Kundt (*Pogg. Ann.* cxlii. 163). According to Cauchy's theory of metallic reflection, based upon experiments by Jamin, the refractive index of metals varies with the angle of incidence, and in most metals the law of dispersion is the opposite of that which holds good for transparent bodies. To put this theoretical deduction to the test of experiment is extremely difficult, and in most cases impossible, on account of the opacity of metals. Kundt, therefore, directed his attention to media standing between metals and transparent bodies, namely the so-called *bodies with surface-colours*, which are transparent for certain rays, but behave to others more or less like metals, and reflect light with metallic lustre. The optical properties of these colouring matters, most of which are strongly tinted, may be summarised, as to all essential particulars, in the statement that the light reflected by them is complementary to that which they transmit, and that the reflected rays are elliptically polarised as in metallic reflection. Hence it appears probable that those bodies exhibit the most general case of dispersion; that is to say, that in them the index of refraction for the ordinary series of rays of the spectrum, diminishing by a wave-length from one end to the other, may increase and decrease in any manner whatever, and even become once or several times less than unity. Christjansson's investigation of fuchsine afforded the first verification of this supposition, which has now been shown by Kundt to hold good for numerous media.

The following bodies, which, in the solid state, have a distinct surface-colour, exhibit in concentrated solution an anomalous dispersion; that is to say, a spectrum in which the order of the colours does not agree with that in the diffraction-spectrum or in the dispersion-spectrum of ordinary bodies: all specimens of aniline-blue and aniline-violet, aniline-green (iodine-green or Hofmann's green), indigo (dissolved in fuming sulphuric acid), indigo-carmino, carthamin (doubtful), murexid (dissolved in potash), cyanine, potassium permanganate, carmine.

All these bodies refract red more strongly than blue light, and in those amongst them in which green is the predominant surface-colour and may still be distinctly recognised in the spectrum, this ray is the least refracted. The substance which exhibits the phenomenon with the greatest clearness is cyanine. Potassium permanganate and carmine exhibit it only when made into a paste by the introduction of solid matter. Kundt further remarks (*Pogg. Ann.* cxliii. 149) that probably all bodies which exhibit anomalous dispersion, and certainly fuchsine, aniline-blue, aniline-violet, aniline-green, murexid, cyanine, and potassium permanganate, are also, in the crystalline state, strongly dichroic; that is to say, a ray of white light entering a crystal of one of these media is resolved by refraction into two rays of different colours.

An objection to the theory above developed has been raised by V. von Lang (*Pogg. Ann.* cxliii. 269) on the ground that the observed appearances are produced in the imperfectly achromatised eye by refraction of the light through the edge of the very acute prisms used in the experiments. Kundt, however (*ibid.* 259), overrules this objection by the description of his method of observation with a telescope, which excludes the possibility of such an influence, and by observations on rays which had passed through the prism at a considerable distance from the edge. Further experiments established the existence of anomalous dispersion in all the substances above mentioned, even in clear solutions of those which had previously been examined only in the pasty condition. The anomaly increases with the concentration. In very concentrated solutions the anomalous spectrum is often very long. The Fraunhofer lines in this spectrum are, for the most part, obliterated by the overlapping of the colours; but they soon appear when one of the colours is intercepted by viewing the spectrum through an absorbent medium. In this way it is seen that individual colours are often extraordinarily elongated, as red in fuchsine and cyanine, green in the latter substance, &c.

Bodies have, for the rays which are strongly reflected by them, and therefore enter into them with comparatively little intensity, and, indeed, for these rays alone, a somewhat considerable coefficient of absorption. In a series of bodies which strongly reflect the middle rays of the spectrum and, at the same time, exert a strong absorp-

tive power on these rays, the refraction increases with extraordinary rapidity in passing from the side of the greater wave-lengths (in air) towards the absorption-band; and in passing from the side of the shorter wave-lengths (in air) to the absorption-band it diminishes with extraordinary rapidity.

In media which exhibit several sharply defined and dark absorption-bands, a refraction anomaly is observed at the edges of each of these bands. Proceeding from the red end of the spectrum, the index of refraction increases strongly on approaching an absorption-band, and diminishes perceptibly behind it. A number of bodies which absorb the spectrum from the blue end onwards exhibit a remarkable increase in the refractive index from the red to the yellow.

Anomalous dispersion has further been shown to exist in solutions of Magdala-red, corallin, alizarin dissolved in potash, orsellin, litmus, iodine in a mixture of chlorine-form and carbon sulphide, logwood (in aqueous or ammoniacal extract), Brazil-wood (ammoniacal extract), blood (red aqueous extract), hæmatin, chlorophyll. Among solid bodies, ammonio-chromic oxalate showed a slight indication of anomaly, and in magnesium platinocyanide, which is doubly refractive, one of the rays exhibited a dark absorption-band in the middle of the spectrum, and indications of anomalous refraction; while, in the other, the absorption affected the whole of the blue and green and extended even into the yellow; this ray accordingly exhibited a great increase of refraction from the red to the yellow.

Anomalous dispersion is likewise exhibited by some bodies which have but a faint surface-colour, such as borax-glass coloured deep blue by cobalt, also potassio-cobaltic and ammonio-cobaltic oxalate (Kundt).

J. L. Soret (*Pogg. Ann.* cxliii. 325) has also made experiments on anomalous dispersion, in which the influence of the solvent was eliminated by immersing the filled hollow prism in a trough with parallel glass sides containing the same solvent. Operating in this manner it is no longer necessary to use light of so great intensity, or to make the light traverse the prism close to the edge. With a moderately strong solution of fuchsin in a prism having a refracting angle of  $30^\circ$ , the violet was scarcely deflected, the red  $15'$ , the orange  $23'$ ; in a much weaker solution the violet was likewise not perceptibly deflected, the red  $6'$ , the orange  $16'$ . Aniline-violet showed only a blue and a carmine-red band, which overlapped each other unless the slit of the spectroscope was very narrow. In sunlight a trace of green was also visible towards the end of the spectrum, on the side of the blue band. The deflection of the blue was  $1'$ , of the red  $4'$ . Potassium permanganate showed a deflection of  $6'$  for violet,  $9'$  for red, and  $12'$  for yellow light. These numbers show to what extent the addition of anomalously dispersive substances diminishes the dispersive power of the solvent without producing much alteration in the mean index of refraction. By successive increase of concentration the dispersive power is first reduced to nothing and then becomes negative.

A theory of dispersion and its anomalies, and their connection with absorption, founded on the consideration of the vibrations produced in the particles of bodies by the vibrations of the ether and their reaction on the latter, has been given by W. Sellmeier (*Pogg. Ann.* cxliii. 272; cxlv. 309, 520; cxlvii. 386, 525).

**Fluorescence.**—1. *Fluorescence of Rarefied Gases after the passage of the Electric Spark.*—According to E. Sarasin (*Ann. Chem. Phys.* [4], xix. 180), oxygen is the only elementary gas which exhibits fluorescence after electric sparks have been passed through it, and among compound gases the only ones which exhibit the phenomenon are those which contain oxygen. Morren, on the other hand (*Compt. rend.* lxxiii. 1033, 1260), maintains that the production of fluorescence requires the simultaneous presence of oxygen and nitrogen either free or combined, and moreover that of an acid. De la Rive (*ibid.* 1237) considers that it still remains a question whether pure oxygen fluoresces well, or whether the admixture of a small quantity of nitrogen is necessary to the production of the phenomenon.

Alvergniat (*Chem. News*, xix. 126) observes that Geissler's tubes become luminous when simply rubbed with the dry hand on a piece of silk. The fluorescence, however, is faint, but increases if the tube contains substances which become fluorescent under electric influence.

F. P. Le Roux (*Compt. rend.* lxxiii. 1104) infers from numerous experiments that the luminosity thus produced is due to electrostatic induction within the rarefied gas. A Geissler's tube becomes luminous in the neighbourhood of a thin plate of ebonite, which is rubbed on the side opposite to the tube. On approaching an electrified body somewhat quickly to a dry glass vessel containing a gas sufficiently rarefied to make it conduct (hydrogen, nitrogen, monoxide, &c.), a very brilliant luminosity is frequently developed; the same effect is produced on removing the electrified body.



regards the mode of action exhibited in these experiments as capable of affording an explanation of certain meteorological phenomena such as the aurora borealis, and 'heat-lightning.'

2. *Fluorescence of Mixtures of Alcohols and Sulphuric Acid.*—A mixture of strong sulphuric acid and absolute ethyl alcohol in equal volumes exhibits, when warmed for ten minutes, a strong greenish-yellow fluorescence, which becomes somewhat stronger on further heating. If the liquid be heated till a large quantity of sulphurous oxide is evolved, and the black pasty mass be then treated with alcohol, the extract still exhibits the same greenish-yellow fluorescence in a lower degree. A mixture of methyl alcohol with strong sulphuric acid becomes yellow-brown when heated and exhibits a strong fluorescence, even if greatly diluted with common alcohol; the upper layer consisting of methyl alcohol remains colourless. Sulphuric acid similarly treated with amyl alcohol becomes first yellow, then orange, and finally crimson with greenish-yellow fluorescence, which becomes more distinct after dilution with common alcohol (F. Goppelsröder, *Zeitschr. anal. Chem.* 1870, 178).

3. *Illumination of Transparent Bodies.*—A. Lallemand (*Ann. Chim. Phys.* [4], xxii. 200) has made observations on the illumination of transparent bodies, observed in directions at right angles to the illuminating ray. The intensity and colour of this illumination differ greatly in different bodies, and if the incident light is polarised, the intensity in each body attains a maximum in the plane of polarisation, and a minimum at right angles to it. Collodion is one of the bodies most capable of illumination quartz (rock-crystal), rock-salt and calc spar are among the least capable. The coefficient of illumination depends upon the chemical nature, molecular constitution, and refracting power of the body. The petroleum hydrocarbons become illuminated the more strongly as their density and index of refraction are greater. In non-fluorescent bodies the lateral light is always completely polarised, and in the direction perpendicular to the plane of polarisation its intensity = 0. Only a very few bodies, however, are found to be quite free from fluorescence, most bodies, even crown and flint glass, exhibiting a coloured fluorescence. This fluorescence is either *isochromatic*, that is, of the same colour as the exciting ray, and in this case may be produced by the corresponding homogeneous ray separated from the spectrum in the ordinary way; or it is *hypochromatic*, and is attended with diminution of the refrangibility; this kind of fluorescence, however, is produced only by the ultraviolet rays. In the case of chlorophyll, the general fact that the loss by absorption of the light which passes through a body arises directly from the number of rays expended in the production of the lateral illumination and the fluorescence, is particularly evident for the red rays of the chlorophyll spectrum absorbed between B and C, which predominate in its fluorescence spectrum. Quinine sulphate, uranium glass, and potassium chromate, and solution of sulphur in carbon sulphide do not extinguish the fluorescent light of chlorophyll; but chlorophyll, on the other hand, completely extinguishes the fluorescence of quinine, and for the most part that of uranium glass, and prevents the conversion of soluble sulphur into insoluble, which is produced in that solution by the more refrangible half of the spectrum (from F onwards).

'At right angles to the plane of polarisation, nearly all isochromatically fluorescent bodies exhibit a light not perceptibly different from white light. The ratio of its intensity to the maximum intensity of the lateral light (parallel to the plane of polarisation) was found to be: in collodion = 0.07, ethyl alcohol = 0.16, amyl alcohol = 0.34, carbon sulphide = 0.60. These ratios are greatly altered by the slightest impurity in the substance, and might serve—as Lallemand's apparatus is very simple—as indications of the purity of the several substances.

On Fluorescence in general, see Hagenbach (*Pogg. Ann.* cxlvi. 65–89, 232–256; 375–406; 508–536; *abstr. Chem. Soc. J.* [2] x. 1058).

On the Fluorescence of Solutions, see H. Morton (*Sill. Am. J.* [3], ii. 198, 355; *Chem. Soc. J.* [2], ix. 392; x. 27).

On the action of Rays of different Refrangibility on Phosphorescent (Fluorescent) Bodies, see E. Becquerel (*Compt. rend.* lxi. 994; *Jahresb. f. Chem.* 1864, 167).

### Absorption.

1. *Absorption of Light by Iodine.*—Iodine vapour, which transmits the blue and red rays of the spectrum, to which property it owes its fine violet colour, absorbs the whole of the red rays as its thickness increases, transmitting only the blue. A solution of iodine in carbon sulphide exhibits the same dichroism when the quantity dissolved is increased; the alcoholic solution, on the contrary, is always red (Andrews, *Chem. News*, xiv. 75).

2. *Absorption of Light by Chlorophyll.*—According to L. Schönn (*Zeitschr. anal. Chem.* 1871, 327) the spectrum of the alcoholic extract of green leaves exhibits only

three absorption-bands, whereas Hagenbach (*Pogg. Ann.* cxli. 245; *Jahresb.* 1871, 171) observed six. Schönn, however, remarks that the absorption-band in the red transmits a little light in the middle, that is to say, it really consists of two bands. In the passage of light through fresh leaves, only the red band was seen at first, but as the leaves dried and faded, the entire spectrum of the alcoholic solution became visible, whence it appears that the solvent does not alter the optical properties of the chlorophyll.

The gold-yellow filtrate of the alcoholic extract treated with soda-ley shows two absorption-bands, one coinciding with the middle of the band in the red, one with the middle of the space between the bands of the orange and red in the unaltered chlorophyll solution.

The blue colouring-matter extracted by alcohol from hyacinths and violets exhibits three absorption-bands all situated a little to the right of those of leaf-green. The solution coloured by acids transmits only red light in a rather thick layer, but in a thinner layer the spectrum brightens from the violet end onwards, and there remains, to the right of the sodium lines, a broad absorption-band which gradually becomes lighter as the solution is more diluted.

The lower side of most green leaves exhibits, when viewed through a hand-spectroscope, a continuous spectrum from B to F, without the absorption-bands peculiar to chlorophyll. The brightness is somewhat less than that of the corresponding part of a spectrum of white paper, but the colours are distributed in nearly the same proportion (J. J. Müller, *Pogg. Ann.* cxlii. 615).

On the Absorption-spectrum of Chlorophyll and its Modifications, see further, pp. 325-330.

**Colours of Bodies.** 1. *Colours of Metals.*—The rays of light reflected from a coloured body are always more or less diluted with white light, because the light which illuminates the surface of the object is never completely decomposed, a portion of it being always directly reflected. The colour of a polished metallic surface is ordinarily invisible, because the tint due to the feeble decomposition of the light is overpowered by the more powerful reflected ray.

The method heretofore adopted for rendering the colour of metals visible, consists in repeatedly reflecting a beam of white light from the metallic surface under examination. At each incidence the white light is partially decomposed, and if the number of incidences be sufficiently multiplied, the whole of the white light will disappear, and only the pure coloured rays be visible. The actual experiment, however, is not very successful, inasmuch as a large portion of the coloured rays is lost by gradual dispersion. A better method consists in bringing into operation the well-known law that when white light is decomposed, the reflected coloured ray is complementary to the transmitted or absorbed ray.

For this purpose a transparent solvent of the metals is required which shall have no chemical action upon them. In the case of the alkali-metals, anhydrous liquid ammonia is found to answer successfully. When placed in this menstruum, these metals gradually dissolve, producing a solution which appears blue by transmitted light. From this circumstance it would appear that the natural colour of the alkali-metals by reflected light is copper-red; and, in fact, on gradually adding the solvent to the metal, the silver-white colour first gives place to copper-red, and then, as the solution becomes more dilute, to the blue colour of the transmitted light. A similar change of colour is exhibited by aniline-blue when treated with alcohol (C. A. Seeley, *Chem. News*, xxiv. 223).

2. *Change of Colour produced by Heat.*—Observations by E. J. Houston (*ibid.* 177, 188) have led to the following general rule: When the natural colour of a body heated in the pulverulent state, without the occurrence of any chemical change (loss of hygroscopic or crystallisation-water included), alters with rise of temperature, and goes through the same changes in the reverse order on cooling, till the original colour is restored, the addition of heat invariably alters the colour towards the red, and the abstraction of heat alters it towards the more refrangible end of the spectrum. Especially sensitive are the following substances, arranged according to the position of their colours in the spectrum:—

**Red:** *Cuprio Ferrocyanide*: colour, mahogany-brown, changed to blackish-brown by heat, the original colour returning slowly on cooling. *Antimonious sulphide* (kermes): brownish-red, becoming darker red-brown. *Anhydrous ferrous ferric oxide*: brownish-red, becoming dark red, brown, black-brown, and finally black at a temperature not much below redness. *Cuprous iodide*: dark red, becoming black at a very moderate heat, afterwards brownish-red, brown, black-brown, and finally almost black, the original colour returning very quickly on cooling. *Mercurous chloride* (cinabar): vermilion-red, becoming brownish-red on heating. *Mercuric iodide*: scarlet-red, becoming black on heating.

coming dark red. *Acid potassium chromate*; red, becoming dark red; best observed on heating a small crystal.

Orange: *Arsenic Bisulphide* (realgar); orange-red in the pulverulent state, becoming red, dark red, and brown; the original colour returns quickly. *Mercuric oxide*: orange-yellow powder, becoming red, dark red, and brownish-red. *Lead iodide*: orange, becoming darker orange, orange-red, and red. *Ferric oxalate*; light orange, becoming darker (in this case only a moderate heat can be applied, as decomposition takes place at higher temperatures).

Yellow: *Neutral Lead Chromate*; yellow-orange, becoming orange-yellow, orange and orange-red. *Stannic sulphide* (mosaic gold); brownish orange-yellow, becoming dark red, nearly black; very sensitive. *Arsenious sulphide* (orpiment); orange-yellow, becoming deeper orange-yellow, yellow [? orange], orange-red, red.

Green: *Argentous iodide*; greenish-yellow, very sensitive; becoming first orange-yellow, then deep orange. *Mercurous iodide*; yellowish-green, still more sensitive than the last; becomes orange-green, reddish-orange, red, and brownish-red in very quick succession.

Many other bodies exhibit similar changes, although less distinctly. No blue, indigo, or violet bodies, have yet been found which, in the solid state, exhibit change of colour before decomposition. Such an alteration has, however, been observed in two white bodies. *Zinc oxide* assumes, when heated, first a scarcely perceptible bluish-white tint, then becomes green and yellowish-green, and does not quite regain its original whiteness on cooling. *Stannic oxide*, when heated, first becomes pale green, then decidedly yellowish-green, and goes through the entire scale of colours to orange and reddish-orange, but returns, on cooling, only to greenish-white.

In solution, bodies are more sensitive to heat than in the solid state. The following have been examined in aqueous solution:—

Red: *Rosaniline*; decidedly red, becomes distinctly darker at the boiling-heat. *Decoction of logwood*; deep red, becoming darker. *Cobaltous chloride*; pale red, becoming darker flesh-red. *Ferric sulphate*; light red, becoming red-brown.

Orange: *Chromic acid*; reddish-orange, becoming redder. *Acid ammonium chromate*; orange-red, becoming pure red. *Ferroso-ferric oxide*; in weak solution orange-red, very sensitive; becomes red and red-brown. *Acid potassium chromate*; orange-red, becoming red.

Yellow: *Ferric nitrate*; brown-yellow, becoming red-brown.

Green: *Potassium ferrocyanide*; yellowish-green, becoming yellow. *Neutral potassium chromate*; yellowish-green, becoming yellow. *Nickel nitrate*; pale green, becoming greenish-yellow. *Nickel sulphate*; green, becoming yellow-green.

Blue: *Cupric chloride*; blue-green, in weak solution becomes decidedly greenish-yellow; very sensitive, the colour returning quickly on cooling. *Cupric sulphate*; decidedly blue, becomes distinctly green at the boiling heat, and quickly recovers its original colour when the source of heat is removed.

Violet: *Ammoniacal Nickel oxide*; violet-blue, becoming light blue. *Litmus solution*; violet, becoming indigo-blue.

The changes of colour produced by fall of temperature were found to be, without exception, directed towards the violet end of the spectrum. *Cinnabar* acquires a bright red colour; *stannic sulphide* changes from brownish orange-yellow to lighter brown-yellow; *mercuric trisulphate* from yellow to greenish-yellow; *lead iodide* from orange to light orange; *lead chromate* from yellow-orange to greenish-yellow. Other bodies exhibited no change of colour, the means adopted for lowering their temperature being, in fact, manifestly inefficient. Aqueous solutions could not, for obvious reasons, be observed at very low temperatures. Distinct results were exhibited only by solutions of—*Cupric sulphate*, pure blue, becoming darker blue on cooling; *potassium ferrocyanide*, nearly pure yellow in saturated solution, becoming slightly greenish; *cupric chloride* changes from bluish-green to blue-green; *ferric chloride*, orange-yellow, becomes yellower; *ferric nitrate*, orange-yellow, behaves like the preceding; *Cupric chloride*, in ethereal solution, cooled by evaporation of carbon sulphide, changed its colour from yellowish-green to pure green.

3. *Complementary Colours*.—A. W. Hofmann (*Dest. Chem. Ges. Ber.* iv. 660) has made observations on the complementary colours exhibited by various aniline dyes in transmitted and reflected light. *Rosaniline* salts in solution exhibit, by transmitted light, a deep purple-red colour; their larger crystals reflect a splendid cantharides green. According to experiments by Dove, these two colours are identical with the complementary colours of a lamina of gypsum, which exhibits, in polarised light, a

difference of path equal to  $\frac{1}{4}$  of a wave-length. A concentrated alcoholic solution of *iodine-green*, evaporated in a glass basin, leaves a homogeneous transparent varnish which transmits a splendid green light, but exhibits by reflected light a highly characteristic rod coppery lustre which comes out very distinctly on friction; these, according to Dove, are the two colours of a gypsum lamina having a difference of path equal to  $\frac{1}{2}$  of a wave-length. On warming the glass dish, the green changes to violet, and the reflected light becomes brass-yellow, corresponding, according to Dove, with a gypsum lamina, having a difference of path equal to  $\frac{1}{2}$  or  $\frac{3}{4}$  of a wave-length.

**Circular Polarisation.**—1. *Relations between Circular Polarisation, Crystalline Form and Molecular Structure.*—Rammelsberg (*Deut. Chem. Ges. Ber.* ii. 31) observes that bodies which exhibit circular polarisation may be divided into three classes: (1) Those which are optically active only in the crystalline, not in the amorphous or the fused state: quartz, sodium chlorate, and sodium bromate, Schlippe's salt. (2) Those which are active only in the amorphous or liquid form, not when crystallised: the two tartaric acids and their salts, the malates, asparagin, various sugars, camphor. (3) Bodies which are active in both states: the only body of this class at present known is strychnine sulphate.

The crystals of circularly polarising bodies are in all cases enantiomorphous, i.e. they exhibit right and left non-superposable forms, resulting from hemihedry. Hence it may be inferred that crystal-molecules are not identical with the individual molecules of bodies themselves, but that a crystal-molecule is a group of individual molecules. In bodies which, in the crystallised form, exhibit the opposition of right and left, the crystal-molecules are linked together in opposite directions (like a right and left handed spiral, screw, winding staircase, snail-shell, or leaf-arrangement). In bodies of the first kind, the individual molecules do not exhibit this opposition of arrangement. In bodies of the third class, on the contrary, this opposition affects the individual molecules themselves, which are arranged in one direction or the other. In bodies of the second class, the molecules constituting a crystal-molecule are arranged in a direction opposite to that of the crystal-molecules, so that in the crystal, the effects of the oppositely arranged individual molecules and crystal-molecules neutralise one another; but when the arrangement of these latter is destroyed by liquefaction or solution, the action of the individual molecules becomes apparent.

On the relation between Circular Polarisation and Crystalline Form, see also P. Groth (*Pogg. Ann.* cxxxvii, 433); V. v. Lang (*ibid.* 447).

2. *Circular Polarisation in Dithionates or Hyposulphates.*—(C. Pope, *Pogg. Ann.* cxxxix, 224). Among the dithionates which crystallise in the hexagonal system, the greatest rotatory power is exhibited by the optically positive crystals of the lead salt with 4 mol. water, and the anhydrous potassium salt, both of which may be obtained in crystals sufficiently large and transparent to admit of the determination of the angle of rotation for the Fraunhofer lines C, D, E, F. The rotation of the plane of polarisation for rays which have traversed the crystal parallel to the principal axis is directed to the right as often as to the left, and is of the same magnitude in both cases. For plates of 1 mm. in thickness the following values were obtained:

	C	Angle of rotation for the line:			
		D	E	F	
Lead Dithionate	4.003°	5.531°	7.252°	8.881°	
Potassium Dithionate	6.182	8.835	10.51	12.33	

The observations on the optically negative dithionates of calcium and strontium presented greater difficulty. The calcium salt with 4 mol. water gave a mean rotation of 2.091; the strontium salt with 4 mol. water gave 1.642. In the double dithionate of lead and strontium, which also crystallises with 4 mol. water, no rotation could be detected; but this negative result was perhaps due to the smallness of the crystals examined. Neither of the four salts above-mentioned exhibited any hemihedral faces which might have afforded indications of the direction of the rotation in the crystal. On the lead salt, however, such faces could be artificially produced by cutting off the proper summits, and leaving the salt to crystallise further. Neither of the salts exhibited circular polarisation when dissolved; neither did the double salt formed of 2 mol. potassium dithionate and 1 mol. sodium chloride, which crystallises in dimetric forms approaching very nearly to the monometric ( $\alpha : c = 0.9356$ ), exhibit the least sign of circular polarisation, even in the thickest crystals.

3. *Circular Polarisation in Benzole and in Camphore.*—Desolaisaux found (*Compt. rend.* lxxiii, 308) that the crystals of benzole, besides their strong double refraction, possess the power of circular polarisation in the direction of their crystallographic axis, and that a plate of this substance 1.15 mm. thick is equal in rotatory power to a quartz plate of 1 mm.; and he has further observed (*ibid.* lxx, 1200) that no such

hedral faces can be detected even on crystals of benzile prepared in the most various ways, and that among the crystals which separate from the solutions, some turn the plane of polarisation to the right, others to the left. When a new solution was formed of dextrogyrate crystals, the first crystals which separated from it were for the most part also dextrogyrate, but those which separated at a later stage were again a mixture of the two kinds. The solution was optically indifferent.

Several kinds of camphor, on the other hand, exhibit circular polarisation in the state of solution, but not when crystallised. Besides common camphor, Descloizeaux has found five other species which possess this property. The following table exhibits the angles of rotation,  $\alpha$ , of these several camphors in alcoholic solution [? saturated], at 17° C. in a column 20 centimeters long:

Patschouli camphor, $C^{15}H^{28}O$ , hexagonal, and exerting negative uniaxial double refraction .	$\alpha = - 237^{\circ}$ at 17°
Mint-camphor or Menthol, $C^{10}H^{20}O$ , hexagonal, negative	$\alpha = - 200^{\circ}$ at 15°
Borneo Camphor, $C^{10}H^{16}O$ , monometric . . .	$\alpha = + 33^{\circ} 4'$
Tercecamphene, $C^{10}H^{16}$ , monometric . . .	$\alpha = - 63^{\circ}$
Monohydrochloride of Turpentine-oil, $C^{10}H^{16}.HCl$ , monometric . . .	$\alpha = - 31^{\circ}$

4. *Circular Polarisation induced by Magnetic Action.*—The rotatory power acquired by a considerable number of liquids under the influence of an electro-magnet has been determined by A. de la Rive (*Phil. Mag.* [4], xl. 393), with the following results:—

1. The specific magnetic rotatory power of a body, *i.e.* the ratio of the rotation produced in it to that which is produced under exactly similar circumstances in distilled water, does not exhibit any definite relation to the other physical properties of the body. Although the denser and more refractive liquids appear for the most part to possess this power in a greater degree than others, there are yet several remarkable exceptions to this rule, amongst which the acids of sulphur are the most conspicuous. Chemical composition, on the other hand, has a decided influence. The entrance of an additional atom of oxygen into a body possessing rotatory power diminishes this power, whereas bromine and iodine increase it greatly, and nitrogen in a lesser degree. This last law is demonstrated especially by observations on certain isomeric compounds. Nevertheless, the atomic grouping, and, therefore, the atomic volume, has also a decided influence.

2. Rise of temperature diminishes the specific rotatory power of all bodies; in the first place, by the expansion and consequent diminution of the number of molecules in a given volume which it produces, and, moreover, by a direct action, independent of expansion, which is especially manifest in slightly expansible bodies, such as water.

3. A mixture of two liquids, formed without the occurrence of chemical action, has a rotatory power which is the mean of those of the constituent liquids. This result does not hold good in the case of mixtures of sulphuric acid and water, if the quantity of one of the two constituents amounts to 0.2 of the mixture. The exception is probably due to chemical combination, which always diminishes the rotatory power. This result may afford a means of distinguishing mere solution from chemical combination.

4. A more exact study of rotatory power promises to throw light on the internal constitution of bodies, inasmuch as the phenomenon depends, not only on the nature of the molecules, but likewise on their arrangement. Solutions and isomeric compounds in particular are likely to furnish important results.

The following are some of the numerical results:—

	Density	Specific rotatory power
Alcohol . . . . .	0.804	0.876
Carbon bisulphide . . . . .	1.270	3.16
Sulphuric acid (concentrated) . . . . .	1.842	0.800
$H^2SO^4$ , chemically pure . . . . .	1.832	0.750

Further, the specific rotatory power of Ethyl Oxide is 0.838; of Ethyl Bromide, 1.200; of Ethyl Iodide, 2.233; of Liquid Sulphur Dioxide, 1.242; of the same in saturated aqueous solution, 1.100; of Copiba-oil, 1.320; of Turpentine-oil, 1.102; of Creasote, 2.259.

**LIGHT, CHEMICAL ACTION OF.** *Distribution of Chemical Energy in the Spectrum.*—Concerning the distribution throughout the spectrum of the intensity in the chemically active rays, Dr. J. W. Draper (*Phil. Mag.* [4], xlv. 422) has professed views opposed to those generally held, according to which a maximum intensity of such rays exists between the lines G and H, and a gradual diminution takes place

on each side of this region. Draper, on the other hand, asserts that, so far from chemical influences being restricted to the more refrangible rays, every part of the spectrum, both visible and invisible, can give rise to chemical changes, or modify the molecular arrangement of bodies; and the ray capable of producing chemical change in any particular substance is that one which the substance has the power of absorbing. The experiments cited by Draper in proof of his conclusions do not appear to be new ones, whilst the fact that different photo-chemically sensitive substances are not affected alike when exposed to the solar spectrum has long been known, and it is also generally admitted that a certain action, though a gradually diminishing one, is noticeable in the case of almost every chemically active substance for a long distance both into the invisible and into the yellow and red rays. The maximum of chemical action, as observed with bromide of silver, differs in position from that with the iodide and chloride, and all these again differ from the maximum (apparently in the yellow) observed in the decomposition of carbonic acid in presence of the green colouring matter of plants.

Thus, for instance, C. Schultz-Sellack (*Deut. Chem. Ges. Ber.* iv. 210) has shown that whilst a collodion-film sensitised with chloride of silver is sensitive for the portion of the spectrum lying half-way between H and G, an iodide-film is sensitive to a point beyond G, and a bromide-collodion to a point close upon F; and Sellack (like Draper) concludes that the haloid silver salts are decomposed by those rays upon which they are capable of exerting a powerful absorbent effect.

Professor H. Vogel, of Berlin (*Deut. Chem. Ges. Ber.* vi. 1302; *Pogg. Ann.* 150, 453; *Phil. Mag.* [4], xlvii. 273) has recently shown that not only is the maximum of photographic action dependent upon the absorbent power of the particular substance for different rays, but that the admixture of certain coloured but chemically inactive substances with the sensitive compound has the effect of altogether altering the position of the maximum of chemical action. Thus, for instance, when a yellowish-red colouring matter, such as aurin, was added in small quantities to a brominized collodion, the plates prepared with this and sensitized in the ordinary way exhibited, when exposed to the solar spectrum and developed, two distinct maxima of action; one (being that observed with an ordinary bromide plate) in the indigo, shading off in intensity on each side, and becoming weak near F; the other (being a new phenomenon) nearly as intense as the first, but occurring in the yellow. Thus it appears possible to prepare a bromide of silver plate which is affected as much by the yellow—usually considered as chemically inactive—rays, as it is with those in the violet, usually supposed to be chemically the most active rays. By adding to the collodion a substance (one of the aniline-greens) which absorbs the red rays between D and C, a bromide-film can be prepared upon which the red rays near C are capable of producing an effect. The sensitiveness of this film was found to diminish from violet to yellow, and then to increase again, showing a distinct maximum at the point where the absorption-band appears in the spectrum of the aniline-green.

Dr. H. Draper (*Phil. Mag.* [4], xvi. 419), in a paper on Diffraction Spectrum Photography, states that he has likewise succeeded in photographing the lines of the visible spectrum from *b* downward, and that the picture comprises not only the regions included within the lines F D, C B, and A, but also the ultra-red rays with their three distinct groups. Draper has not, as yet, made known the process by which he has obtained these singular and important results.

E. Budde (*Phil. Mag.* [4], xlii. 290, 204) has described an experiment in which an increase of volume was observed when chlorine was exposed to the chemically active rays, and a corresponding contraction when no longer under the influence of light. A Leslie's differential thermometer was filled with chlorine, and oil of vitriol previously saturated with chlorine substituted for the index fluid. The bulbs were then placed so that either of them could be illuminated by any portion of the solar spectrum, while the variation in the position of the index was observed by a telescope. A small expansion of the gas occurred when the bulb was exposed to the red and yellow rays, but a maximum displacement of 6-7 millimeters took place in the blue and ultra-violet rays. Control experiments showed that this change of volume was not due to change of temperature. A thermometer filled with chlorine was kept in a water-bath and exposed to direct sunlight. By alternately shading the one and the other of the bulbs, a displacement of the index amounting to several centimeters was obtained. Budde explains this expansion by supposing that the light actually decomposes chlorine-molecules into chlorine-atoms. The writer of this article thinks it right to observe that he has repeated Budde's experiments, but that he has failed to obtain the slightest alteration in volume in the insulated as against the non-insulated portion.

With respect to the measurement of the chemical action of light, little has been done beyond the establishment of a self-acting method applicable to observations. Roscoe has recently described (*Phil. Trans.* 1874, Part II.; *Pogg. Ann.* xl. 244; *abstr.*

*Proc. Roy. Soc.* xxii. 158) an instrument by which the varying intensity of the chemically active rays, as affecting chloride of silver paper of constant sensitiveness, can be made self-recording. The method described (iii. 686) in the Bakerian Lecture for 1865, although it has been the means of bringing into notice many important facts concerning the distribution of the sun's chemical activity throughout the atmosphere, as well as in different situations on the earth's surface, has not as yet been introduced as a portion of the regular work of meteorological observatories, owing to the fact that, in order to obtain a satisfactory curve of daily chemical intensity, at least hourly observations need to be made, and this involves the expenditure of more time and labour than it has been found possible to give. The present method, whilst preserving untouched the principles and accuracy of the former method, reduces the personal attention needed for carrying out the measurements to a minimum, and thus renders its adoption in observatories possible.

According to this plan, a constant sensitive paper is exposed by a self-acting arrangement for accurately known times, at given intervals throughout the day. The insolation apparatus stocked with sensitive paper is placed in position either early in the morning of the day during which the measurements have to be made, or on the previous night, and by means of an electric communication with a properly arranged clock, the sensitive paper is exposed every hour during the day, so that, in the evening, the observer has only to read off, in the ordinary manner, the hourly intensities which have been recorded on the paper during the day.

This self-recording arrangement, though apparently simple, involves points which have rendered its successful completion a somewhat difficult matter, owing, in the first place, to the great variations which occur in the chemical intensity of total daylight in different places, at different times of the day, and in different periods of the year; and secondly, owing to the fact that, in order to be able to estimate the chemical intensity, the coloration acquired by the paper must reach, but not much exceed, a given tint. It becomes necessary, therefore, that on each occasion when an observation is needed, the sensitive paper should be exposed mechanically, not once, but for several known but varying intervals of time, quickly succeeding each other; so that whatever may be the intensity of the total daylight (supposed during these intervals to remain constant), some one at least of the several exposed papers will possess the requisite shade. This is accomplished by a duplicate arrangement of a clock and insolation-apparatus, by means of which discs of the constant sensitive paper are exposed each hour for successive known intervals of time, varying from two to thirty seconds. After an interval of an hour, another set of discs are exposed for the same series of intervals, and these series of insolutions are repeated once every hour during the day. The mechanical arrangements for effecting this with accuracy are shown in the following figures. The minute-hand A of the clock (fig. 22.) is connected with the train of wheels B, C, D, in such a manner that the last wheel D makes one revolution in two minutes. On the periphery of the metal wheel are fixed eleven stout platinum needles (numbered 1 to 11 in the figure), each of which projects three millimeters beyond the face of the wheel. As the wheel turns round, each of these needles is successively brought in connection with the elastic metal arm E, the end of which is coated with platinum. The platinum pins are attached to the wheel in such a manner that the contact lasts only for an instant, and is then broken till the next pin comes into position. This takes place eleven times in all. The intervals during which the contact is broken are of various lengths, according to the intervals between the platinum pins. In this country the following times of breaking contact have been found the most convenient:—

Interval	No. 1	2	3	4	5	6	7	8	9	10
Seconds	2	3	4	5	7	10	12	17	20	30

If the instrument is to be used in places where the chemical intensity is much greater or smaller, another interval must be adopted. While the wheel is in contact with the elastic arm E, an electric current from several cells of a powerful battery passes through a second elastic arm F, and through wires which connect the clock with the insolation-apparatus. As soon as contact is broken at E, this current is likewise interrupted. The paper of constant sensitiveness is cut into long narrow strips as in Morse's telegraph-apparatus. The length (about 3 meters) must be sufficient for a day. This paper strip is wound round the roller B (fig. 23) from which it passes over the light metal wheel W, having a diameter of about 16 centimeters. One end of the paper strap is attached to this end. The escapement wheel F (fig. 23) is set in motion by a spring S, and has a common axis with the wheel W. The escapement is connected with a piece of iron K, placed near an electromagnet M, round which a current passes as soon as metallic contact is established with E (fig. 22).

When a current passes round the electro-magnet, the piece of iron K is attracted,

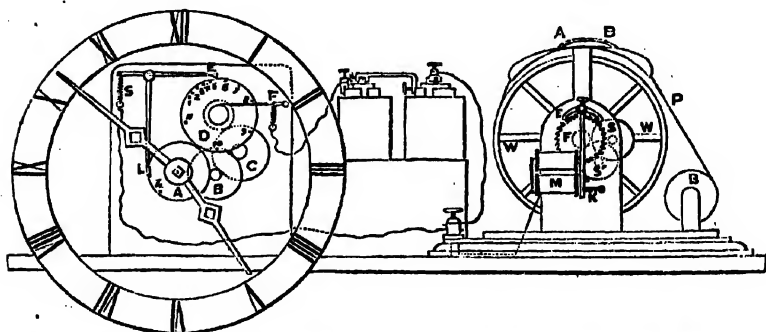
the escapement is set free, and the wheel with the paper is moved through an arc depending on the number of teeth in the escapement-wheel F. As soon as the current is interrupted, the piece of iron is brought back to its original position by the spiral spring S.

When the minute-hand of the clock (fig. 22) comes to a certain point, a pin *p*, fixed upon it, presses on the longer arm of a lever L, which depresses the elastic arm E. The platinum pins of the wheel D now press against the arm E, and the current is established and interrupted in the intervening spaces. The sensitive paper is thereby moved forward, after certain intervals, through a distance which is sufficient to bring a fresh part of it under the circular opening. This small paper disc (4 mm. in diameter) is thereby exposed till the current is re-established, and a fresh disc brought under the opening. It is easy to see that by this means the sensitive paper is exposed during the above-mentioned interval, which may amount to 80 seconds, till the wheel D has made one revolution. The fixed pin *p*, of the minute-wheel, has, during this interval, moved forward so far that it no longer presses against the bent and thick end of the lever L, and consequently the end of the elastic arm E is brought back by the insulated spiral spring S. The arm now remains in this position for an hour, when it is again pressed down and brought into connection with the platinum pins. During this hour a disc of paper is exposed and thereby strongly blackened. If one of these black discs is marked in the course of the day, the hours may be known in which the different expositions have taken place.

The apparatus, when in use, is protected by a light metallic blackened shade, on which is fixed a metallic plate with a circular opening (4 mm. in diameter) carefully rounded on the edges. A steel spring AB (fig. 23), on which the sensitive paper is

FIG. 22.

FIG. 23.



pressed, presses it against the horizontal metal plate, so that the exposed paper disc lies close under the aperture of the plate. To keep the paper and apparatus dry during wet weather, the whole is covered with a glass shade. The loss of light thereby occasioned must be experimentally determined for each instrument.

When the apparatus is taken out in the evening, which must be done in a room lighted by a soda-flame, the black discs are seen which have been exposed for an hour. Between these are ten discs of various shades; that which has been exposed for 2 seconds only is perhaps scarcely visible, while that which has been exposed for 80 seconds is perhaps too dark for the determination of the intensity. One of the discs must have a shade whose intensity can be read off on a graduated strip (see vol. iii. p. 687; figs. 705, 706).

A new method of calibrating the fixed strips of standard tint necessary for these measurements is also described, but for this we must refer to the original paper.

This paper also contains graphic representations by curves of the results of a series of comparisons of the curves of daily chemical intensity obtained (1) with the hand-insulator; (2) with the self-recording instrument. Comparisons of this nature were made during the months of May, June, and July, 1873, by simultaneous hourly determinations in the neighbourhood of Manchester, according to both methods. The tables and curves show the close correspondence of the two sets of observations. The integrals of total chemical intensity deduced from the two sets of observations likewise exhibit as close an agreement as can be expected from the nature of the experiments.

H. E. R.



**LIGNIN.** This name is sometimes used synonymously with cellulose (i. 818), but it is more properly applied to the substance, or mixture of substances, which ferments and encrusts the cellulose framework of many vegetable tissues. This encrusting matter, which may be removed by prolonged digestion with dilute nitric acid, contains more carbon than cellulose, and more hydrogen than oxygen, whereas in pure cellulose the hydrogen and oxygen are in the proportion to form water. Lignin is much less digestible than cellulose, and forms indeed the indigestible part of fodder (Payen, *Compt. rend.* lxxii. 457).

**LIGNITE.** The composition and heat of combustion of lignites from several localities in France and Germany have been determined by A. Scheurer-Kestner and C. Meunier (*Compt. rend.* lxxiii. 1332), with the following results:

I. Hard lignite from Fadaeu (Bouches-du-Rhône): black compact mass, with dull conchoidal fracture.

II. Rich lignite from Manosque (Basses-Alpes): friable mass, having an unctuous aspect, black colour, and uneven fracture.

III. Hard lignite from Manosque: black compact mass, with shining conchoidal fracture.

IV. Rich lignite from Bohemia: compact mass, with uneven fracture, black and shining.

V. Lignite passing into fossil wood, from Bohemia: aspect dull in the direction of the woody fibres, shining in the transverse direction. The fracture displays a stratification of closely lying layers.

VI. Fossil wood passing into lignite: much resembles the preceding.

	I.			II.			III.		
	Crude	Pure	Volatile part	Crude	Pure	Volatile part	Crude	Pure	Volatile part
Water . . .	8.27	—	—	1.00	—	—	7.82	—	—
Carbon . . .	55.30	72.98	25.78	55.26	70.57	13.91	56.68	66.31	36.75
Hydrogen . . .	3.06	4.04	11.09	4.26	5.44	10.37	4.15	4.85	9.10
Oxygen . . .	17.41	22.98	63.13	18.78	23.99	45.72	24.65	28.84	54.15
Ash . . .	15.96	—	—	20.70	—	—	6.70	—	—
	100	100	100	100	100	100	100	100	100
	Heat-units			Heat-units			Heat-units		
Heat of combustion observed . . .	6483			7363			6991		
„ calculated by Dulong's law . . .	6295			6533			5782		
Sum of heats of combustion of elements . . .	7270			7551			7006		

	IV.			V.			VI.		
	Crude	Pure	Volatile part	Crude	Pure	Volatile part	Crude	Pure	Volatile part
Water . . .	2.39	—	—	10.41	—	—	10.60	—	—
Carbon . . .	72.03	76.58	68.95	67.06	66.51	32.56	67.72	67.60	33.28
Hydrogen . . .	7.78	8.27	10.97	4.05	4.72	9.50	3.89	4.55	9.38
Oxygen . . .	14.24	15.15	20.08	24.68	28.77	57.94	23.78	27.85	66.34
Ash . . .	3.66	—	—	3.80	—	—	4.01	—	—
	100	100	100	100	100	100	100	100	100
	Heat-units			Heat-units			Heat-units		
Heat of combustion observed . . .	7924			6358			6311		
„ calculated by Dulong's law . . .	8343			5759			5827		
Sum of heats of combustion of elements . . .	8267			6970			7010		

The heat of combustion is in all cases less than the sum of the heats of combustion of the elements, carbon and hydrogen. In this respect the lignites are distinguished from coal, which always gives a calorific power greater than that of the carbon and hydrogen. It is impossible, therefore, to judge of the value of a combustible of this kind from its elementary composition.

A lignito from Vescovado in the province of Sienna, Italy, was found by E. Kopp (*Moniteur Scientifique*, 1870, 58) to contain 26.48 p.c. volatile combustible matter, 45.52 non-volatile combustible matter, 21.80 water, and 9.20 ash. By coking in a retort it yielded 51.72 p.c. of coke. It contained 1.86 p.c. sulphur.

**Action of Alkalis on Lignite.**—Lignite from Traunthal fused with three times its weight of caustic potash yields a crystalline sublimate of pyrocatechin; but this product is not obtained if the lignite has been previously exhausted with ether: hence it appears that the pyrocatechin is formed from the bitumen of the lignite. Pyrocatechin is likewise obtained from other lignites, but only from those which exhibit a distinct ligneous structure. Lignites of the older formations do not yield it, and coal is not acted upon at all by fusion with alkalis (Schinnerer and Morawski, *Deut. Chem. Ges. Ber.* v. 185).

On the Gases enclosed in Lignite, see COAL (p. 361).

On the Transformation of Old Timbering into Lignite in the rubbish of the Dorothea Mine, at Clausthal in the Upper Harz, see Hirschwald (*Jahrb. f. Mineralogie*, 1874, 204; *Chem. Soc. J.* [2] xii. 670).

**LIME-TREE.** On a Saccharine Exudation from the Leaves of a Lime-tree, see MANNA.

**LIQUIDS.** On the Constitution of Liquids, see Handl (*Wien. Akad. Anzeig.*, 1872, 88; *Chem. Centr.* 1872, 433).

On the Distillation and Boiling Points of Liquids, see DISTILLATION (pp. 436-438).

On the Capillarity-Constants and Surface-tension of Liquids, and the Spreading of one Liquid on the Surface of Another, see CAPILLARITY (pp. 240-240).

**Specific Gravity of Liquids.**—An exact and easy method of determining the specific gravity of liquids is given by H. Sprengel (*Chem. Soc. J.* [2], xi. 577). The

FIG. 22.

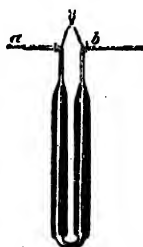


FIG. 23.



apparatus used consists of an elongated U-tube (fig. 22), the open ends of which terminate in two capillary tubes, which are bent at right angles in opposite directions. The size and weight of the instrument must be adapted to the size and capability of the balance in which it is to be weighed. As the ordinary balances indicate  $\frac{1}{10}$  milligram when loaded with 50 grams, the U-tube, when charged with the liquid, should not exceed this weight (1,000 grains = 64,709 grams). An instrument used by Dr. Sprengel had a length of 17.7 cm. (7 inches), and was made of a glass tube, the outer diameter of which was 11 mm. ( $\frac{1}{2}$  of an inch). The U-shape is of course adopted for the sake of presenting a large surface, and so rendering the instrument sensitive to changes of temperature. An important point is the different calibre of the two capillary tubes. The shorter one is a good deal narrower (at least towards the end) than the longer

one, the inner diameter of which is about  $\frac{1}{4}$  mm. The horizontal part of this wider tube is marked near the bend with a delicate line (*b*). This line and the extremity of the opposite capillary tube (*a*) are the marks which limit the volume of the liquid to be weighed.

The filling of the instrument is easily effected by suction, the little bulb apparatus (as represented in fig. 23) having previously been attached to the narrow capillary tube by means of a perforated stopper, i.e. a bit of an india-rubber tube tightly fitting the conical tubulus of the bulb. On dipping the wider and longer capillary tube into a liquid, suction applied to the open end of the india-rubber tube will produce a partial vacuum in the apparatus, causing the liquid to enter the U-tube. As this partial vacuum maintains itself for some time (on account of the bulb, which acts as an air-chamber), it is not necessary to continue the suction if the end of the india-rubber tube be timely closed by compression between the fingers. When bulb and U-tube have about equal capacity, it is hardly necessary to repeat the exhaustion more than once during the filling. Without such a bulb the filling of the U-tube through these fine capillary tubes is somewhat tiresome. The emptying of the U-tube is effected by reversing the action and so compressing the air.

After the U-tube has been filled, it is detached from the bulb, placed in water of the standard temperature almost up to the bends in the capillary tubes, left there until it has assumed this temperature, and, after a careful adjustment of the volume, it is taken out, dried, and weighed.

Particular care must be taken to ensure the correctness of the standard temperature, as a mistake of  $0.1^{\circ}$  causes the weight of 10 c.c. of water to be estimated either too high or too low by 0.14 milligram, giving rise to an error in the 5th decimal, or making 100,000 parts 100,001.4 parts.

A peculiar feature of the instrument is the ease and precision with which the measurement of the liquid can be adjusted at the moment it has taken the standard temperature, the liquid expanding and contracting only in the wider capillary tube, viz., in the direction of the least resistance. The narrow capillary tube remains always completely filled. Supposing the liquid reaches beyond the mark *b*, it may be reduced through capillary force by touching the point *a* with a little roll of filter-paper. Supposing, however, that in so doing too much liquid is abstracted, capillary force will redress the fault if the point *a* be touched with a drop of the liquid under examination: for this gentle force acts instantly through the whole mass of the liquid, causing it to move forward again to the mark or beyond it.

As the instrument itself possesses the properties of a delicate thermometer, the time when it has reached the standard temperature of the bath may be learned from the stability of the thread of liquid inside the wider capillary tube. The length of this thread remains constant after the lapse of about five minutes.

In wiping the instrument (after its removal from the bath) care should be taken not to touch the point *a*, as capillarity might extract some of the liquid; otherwise the handling of the instrument requires no especial precaution.

The capillary tubes need not be closed for the purpose of arresting evaporation, at least that of water. It appears from the mean of several determinations that the error arising from this source amounts in one hour to  $\frac{1}{100}$  milligram.

If the temperature of the balance-room is high, and the expansion of the liquid considerable, it may be found necessary to put a small cap (bowl-shaped and open at both ends) over the extremity of the wider capillary tube, for the purpose of retaining the liquid which, during the time of weighing, might otherwise be lost, owing to its expansion. Raising the standard temperature of the bath is another way of meeting this inconvenience. When a cap is used, the wider capillary tube need not be longer than the narrow one.

For Marignac's determinations of the specific gravities and expansions of aqueous solutions, see HEAT (pp. 602-604).

Extensive Tables of the Specific Gravities of the Aqueous Solutions of various Salts used in the Arts and Manufactures are given by Benno Franz (*J. pr. Chem.* [2]. v. 274-308).

For Thomson's determinations of the Specific Gravities, Molecular Volumes, and Specific Heats of Solutions, see HEAT (pp. 596-600). For Marignac's determinations of the Specific Heats of Solutions, pp. 600-602.

On Conduction of Heat in Stratified Liquids, p. 640.

*Compressibility of Liquids under High Pressures.*—The following determinations are by Chaillet (*Compt. rend.* lxxv. 77):—

	Density	Temperature	Compressibility corresponding to one atmosphere	Total pressure applied: Atmospheres
Distilled water deprived of air	1000	+ 8	0.0004451	705
Carbon bisulphide . . . . .	—	+ 8	0.0000980	607
		+ 9	0.0000676	174
Alcohol . . . . .	0.858	+ 9	0.0000701	305
		+ 11	0.0000727	680
Petroleum . . . . .	0.865	+ 11	0.0000828	610
Essence of petroleum . . . . .	0.720	+ 10.5	0.0000981	630
Ether . . . . .	—	+ 10	0.0001440	630
Sulphurous acid . . . . .	—	- 14	0.0003014	606

These numbers are not corrected for the compression of the glass vessel, for the determination of which, under these high pressures, no method is known.

**Transpiration of Liquids.**—Löwenthal (*Zeitschr. anal. Chem.* x. 298) has made experiments on the capillary transpiration of certain liquids, by means of an apparatus differing only in a few details from that used by Graham (iii. 722). The vessel containing condensed air has a capacity of not less than 1,500 c.c., and two capillary tubes are used, fitted with two stopcocks of exactly equal dimensions, so that two experiments may be carried on simultaneously. Instead of placing the tubes in water at a known temperature, Löwenthal finds it easier to regulate the temperature of the room so that it shall be maintained at a constant point during the experiments. The tubes used are of varying capacity, containing from 2.5 to 57 c.c., some of these having one and some two bulbs. The time which the liquid takes to pass through the capillary tube is noted by a method similar to that employed by Graham.

Löwenthal finds that the fatty oils used in the arts have very different rates of transpiration, and that this is also the case with milk, beer, wine made from fruits, grape-wine, and various other substances. This fact may perhaps be turned to practical account in testing such compounds.

The experiments show further that, for at least some liquids, there exists a relation between their respective diffusion and transpiration rates. Thus, Graham gives the diffusion of HCl solution to NaCl solution as 1 : 0.7, Löwenthal has found their respective rates of transpiration to be as 1 : 0.732. In like manner the diffusion of NaCl to sugar is as 2.33 : 7, their transpiration rates as 2.33 : 5.83.

**LITHIOPHORITE** (A. Frenzel, *J. pr. Chem.* [2], iv. 353; *Jahresb. f. Mineralogie*, 1872, 219). This mineral, nearly allied to the cupriferous and cobaltiferous ores of manganese, contains 1.5 p.c. lithia. It is found, usually on quartz, in the beds of iron ore of the granite district near Schneeberg, Schwarzenberg, and Johanngeorgenstadt. The felspar of the granite, which is much weathered, contains a trace of lithium, recognisable by the spectroscope. The mica contains more of this metal.

Lithiophorite is amorphous, occurs in compact, botryoidal, and reniform masses, in flat shell-like forms, and in pseudomorphs after calcspar. Hardness = 3; sp. gr. = 3.14–3.36. Colour, bluish-black; streak, brown-black. It gives off water when heated in a tube; does not melt before the blowpipe, but colours the flame with carmine-red.

Two analyses, by C. Winkler, of lithiophorite from Schneeberg, gave:—

	K <sup>2</sup> O	Li <sup>2</sup> O	BaO	CoO	NiO	CuO	MnO	O	Fe <sup>2</sup> O <sup>3</sup>	Al <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O	X*
(1.)	0.73	1.23	2.78	2.42		1.74	55.12	10.28	1.48	10.54	12.64	— = 98.96.
(2.)	1.50	1.42	1.26	0.64	0.30	0.96	40.87	7.77	2.43	15.53	15.42	3.08 = 100.18.

\* Sand; also traces of lime, and in (1.) of bismuth oxide.

F. v. Kobell has detected lithia in the asbolans of Sayn, and of the iron mine at Siegen.

**LITHIUM.** This metal, like potassium and sodium, dissolves in anhydrous liquid ammonia, and is left behind, with its original appearance and colour, on evaporating the liquid (Seeley, p. 60).

On the Spectroscopic Character of various Lithium Minerals, see F. v. Kobell (*J. pr. Chem.* [2], iii. 176; *Chem. Soc. J.* [2], ix. 312).

**Separation of Lithium and Sodium.**—To separate these metals, v. Kobell (*J. pr. Chem.* [2], v. 112) heats the mixed chlorides to incipient fusion in a weighed platinum crucible; then weighs the mixture, leaves it exposed for 24 hours to an atmosphere not moist enough to act upon the sodium chloride, till the lithium chloride has absorbed water; drenches the partly deliquesced mass with alcohol; decants carefully; repeats the washing and decantation a second time; and weighs the residual sodium chloride. An experiment on weighed quantities of the mixed chlorides showed that the method gives exact results.

**Lithium Hydrate.**—An aqueous solution of lithia evaporated in a vacuum yielded a slightly hygroscopic hydrate,  $\text{LiHO.H}^2\text{O}$  (Muretow, *Deut. Chem. Ges. Ber.* v. 331).

**LOBARIC ACID.** A resinoid acid obtained from the lichen called *Parmelia saxatilis* by Wallroth, *Loberia adusta* by Hoffmann. It is colourless, crystallises in warty masses made up of thin plate, and in its degree of solubility in different menstrua and in other of its properties, it resembles a crystalline resin. It is not affected by prolonged exposure to ammonia gas, but dissolves in either aqueous or alcoholic ammonia, forming a colourless solution, which turns rose-red on exposure to the air, and dries up to an amorphous violet-brown mass, resembling in tint the thallus of the lichen which yields it. It dissolves in caustic potash with a pure yellow colour, which, on exposure and evaporation, changes like the ammonia-solution to rose-red and brown-violet. When heated it fuses, evolves dense inflammable vapours, and chars. It has the composition expressed by the formula  $\text{C}^{17}\text{H}^{10}\text{O}^3$ , that of evernic acid being  $\text{C}^{17}\text{H}^{10}\text{O}^2$ .

The colour of the brown variety of *Parmelia saxatilis* may, perhaps, be attributed to the presence of oxidation-products of the potassium salt of lobaric acid. The colour is only superficial, and is produced by the action of the potash derived from the weathering of the granite upon which the lichen grows (W. Knop, *Chem. Centr.* 1872, 172).

**LOKAO.** This dye, also called *Chinese green*, was originally imported from China, but has likewise been obtained from the berries of the common buckthorn. In the crude state it is a lake containing 25 p.c. of mineral matter. If left in contact with water for some days it ferments, and is partially reduced. The liquor is filtered, and the residue washed with cold water, and dissolved in warm water, which it colours reddish-violet. This solution, on exposure to air, throws down a blue precipitate, which, though purer than the original lokao, still leaves a considerable ash on ignition. Perfectly pure lokao is obtained by agitating the crude green with solution of ammonia carbonate, filtering, precipitating with alcohol, washing, and drying at  $100^\circ$ . The product is blue (confirming the observation of Persoz, that 'Chinese green, when quite pure, is a blue'), and is a compound of ammonia with the pure colouring matter (*lokaïn*). The analysis of ammonium-lokaïn gives numbers corresponding with the formula  $(\text{NH}_4)^2\text{C}^{20}\text{H}^{10}\text{O}^{14}$ . Lokaïn may be considered as a weak acid, and represented by the formula  $\text{C}^{20}\text{H}^{10}\text{O}^{14}$ .

When ammonium-lokaïn is kept at  $100^\circ$  for some hours, it is transformed into an insoluble violet substance, which is also formed when crude lokao is fermented with yeast, but is best obtained by treating ammonium-lokaïn with warm dilute sulphuric acid, when it splits up into glucose (showing that lokaïn is a glucoside), and an insoluble residue (*lokaëtin*), the composition of which may be expressed by the formula  $\text{C}^{19}\text{H}^{10}\text{O}^{10}$ ; and the contact of this substance with a trace of ammonium-carbonate, produces the violet before named (*ammonium-lokaëtin*).

Lokaëtin, when heated with dilute nitric acid at  $100^\circ$ , splits up into oxalic acid and a substance giving an intense yellow coloration with alkali. With concentrated sulphuric acid lokaëtin is changed into a substance giving a deep blue with weak alkali. Its formula is  $\text{C}^{18}\text{H}^{12}\text{O}^8$ , i.e., lokaëtin minus  $2\text{H}^2\text{O}$ .

**Uses of Lokao, &c., in Dyeing.**—(1.) The liquor obtained by digesting crude lokao with water, and filtering, dyes cotton a pale green, but gives to wool and silk only a very pale bluish-grey, similar to the tint of some silks dyed by the Chinese. (2.) The deep violet ammonium-lokaëtin may be fixed upon cotton without a mordant, also upon silk and wool. (3.) Ammonium-lokaëtin, added to a bath of sodium thiosulphate, gives a liquor which dyes cotton a very pure sky-blue, permanent in sunlight, and fast when washed.

**LÜNEBURGITE.** This name is given by C. Nöllner (*Münch. Acad. Ber.* 1870, i. 291) to a mineral obtained by boring at Lüneburg. It contains—besides 0.7 p.c. BF<sub>3</sub>, which goes off at a red heat, and traces of salts from the neighbouring salt bed—the components given under A, agreeing nearly with the formula  $(2\text{MgO.H}^2\text{O.P}^2\text{O}^5) + (\text{MgO.B}^2\text{O}^3) + 7\text{H}^2\text{O}$ , which requires the numbers B:—

	MgO	FeO <sup>a</sup>	B <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O	
A (found)	25.3	29.8	12.7	32.2	= 100
B (calc.)	25.10	20.83	14.32	30.25	= 100

The same composition was exhibited by some crystals deposited from the mother-liquors of sen-water, the source of which is not given (Nöllner, *Jahrbuch f. Mineralogie*, 1871, 175).

**LUPINE.** The general composition of yellow and blue lupine-seed is as under:—

	Yellow lupine	Blue lupine
Water	10.4	13.2
Albuminoids	37.5	22.0
Non-nitrogenous extractive matter	27.3	43.8
Fat	4.4	5.6
Crude fibre	16.4	12.2
Ash	4.0	3.2
	100.0	100.0

As lupine-seed is rich in nutritive matter, and can, moreover, be grown on a poor soil, it would be of great value as feeding material but for the bitter principle (the volatile alkaloid) which it contains. The presence of this substance renders lupine-seed distasteful and injurious to animals, especially to pigs; sheep are but little affected by it. The blue lupine-seed is more objectionable than the yellow. The amount of alkaloid present varies a good deal. The alkaloid may be more or less removed by baking the seed in an oven or kiln; or by steeping in water and washing; or by treatment with dilute hydrochloric acid, washing, and then boiling with a little sodium carbonate (H. Settegast, *Ann. d. Landwirtschaft. Wochenblatt*, June 7, 1871).

Yellow lupine-seed has been further examined by A. Beyer (*Landwirtschaftliche Versuchs-Stationen*, xiv. 161). He finds that a section of the moist seed is strongly acid to litmus-paper, and that the seed contains citric acid. Ritthausen (*J. pr. Chem.* [2], ii. 330) found malic and oxalic acids.

Beyer also found a viscid substance, soluble in alcohol, but did not succeed in obtaining it pure.

The seed contains two fats: a fluid fat extracted by cold ether, and a solid fat obtained by treatment with hot alcohol after the extraction by ether. The percentage composition of the fluid fat, when purified, is 75.7 C., 11.35 H., 0.098 P., 12.862 O.; while that of the solid fat is 72.68 C., 10.84 H., 1.56 P., 14.92 O. The amount of phosphorus in the solid fat (quite free from adhering phosphates) is remarkable. Knop found 1.25 p.c. of phosphorus in a fat from a sugar-pea.

The alkaloids of lupine-seed are best extracted by means of alcohol containing hydrochloric acid; when isolated they are found to be fluid bodies resembling conine. Beyer separates the alkaloids by the different solubility of their platinum salts. The platinum salt, insoluble in alcohol and in cold water, has the formula  $C^{11}H^{12}N^2O^2Cl^2.PtCl^4$ ; the more soluble platinum salt has the formula  $C^{20}H^{16}N^2O^2Cl^2.PtCl^4$ . The soluble platinum salt corresponds with an alkaloid soluble in water, and *vice versa*.

Siewert has separated the two alkaloids by distillation. The one distilling at 216° corresponds with the insoluble platinum salt; that distilling at 261° with the soluble. Siewert's formulae for the alkaloids are in each case less, by a molecule of water, than those deduced from the above platinum salts.

**LUTEIC ACID.** A yellow colouring matter prepared from the flowers of *Euphorbia Cyparissias* (p. 495).

**LUTIN.** This name is given by Thudichum (*Proc. Roy. Soc.* xvii. 263) to the yellow substance obtained by Piccoli and Lieben from the ovary of the cow, and called by them hæmolutein (1st *Suppl.* 497).

**LUTECOBALTIC CHLORIDE.** See COBALT-BASES, AMMONIACAL (p. 365).

**LUTIDINE.** This base has been found, together with several of its homologues, in tobacco-smoke (see TOBACCO).

**LYCOCTONINE.** See ACONITE ALKALOIDS (p. 24).

## M

**MAGNESITE.** Crystals of magnesite from Mariazell in Styria, some colourless, others brownish, exhibit, according to J. Rumpf (*Jahrbuch. f. Mineralogie*, 1870, 356) the form OR,  $\infty P2$ .

Magnesites (a) from Mahronberg in Styria, sp. gr. 2.091–2.094; (b) from Frankenstein in Silesia, sp. gr. 2.090, have been analysed by H. Schwarz (*Dingl. pol. J. exxviii*, 154), with the following results:—

MgCO <sup>3</sup>	CaCO <sup>3</sup>	* FeCO <sup>3</sup>	Insol.
92.52	3.55	3.79	0.14 = 100
98.47	trace	trace	1.53 = 100

A ferruginous magnesite from the north bank of the Schuylkill river, between Philadelphia and Montgomery county, Pennsylvania, consists, according to Leeds (*Chem. News*, xxii, 173), of:—

MgO	FeO	CaO	CO <sup>2</sup>
38.43	10.39	3.20	47.96 = 100.07

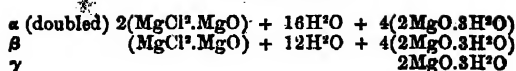
**MAGNESIUM.** *Separation from the Alkali-metals.*—The following method is given by H. Scheerer (*J. pr. Chem.* [2], iii, 4761). Evaporate the hydrochloric acid solution of the metals nearly to dryness in a platinum crucible; add ammonium oxalate; dry, heat gently, then to full redness; treat the residue with water, boil and filter. Magnesium carbonate is then found on the filter, potassium and sodium carbonates in the filtrate. This method is said to yield good results. If, however, the metals are present wholly or partly as sulphates, these salts must first be converted into chlorides by treatment with barium chloride.

*Separation from Aluminium.*—When a solution containing alumina and magnesia, together with a large quantity of sal-ammoniac, is boiled with excess of ammonia till all the ammonia is driven off, alumina is thrown down almost free from magnesia. If, however, sulphuric acid is present, the quantity of magnesia precipitated, together with alumina, is greater than when that acid is absent. The quantity of magnesia in the precipitate likewise increases when the ammonia is added quickly and in excess, instead of being added in drops and with stirring. In solutions containing sulphuric acid, rapid addition of ammonia leads to the precipitation of 2 mol. magnesia with each molecule of alumina, whereas, when the ammonia is gradually added, the precipitate contains only 1–2 p.c. magnesia (*S. Wrinkles, Chem. News*, xxii, 4).

*Oxychlorides.*—Sorel found that a mixture of strongly heated *Magnesia usta* with a concentrated solution of magnesium chloride dries up in a few hours to a hard mass, apparently of oxychloride, which resists the action of water (1st Suppl. 796). The products thus formed have been more exactly investigated by C. Bender (*Ann. Ch. Pharm.* clix, 341), whose analysis of a sample prepared as above and hardened by six months' exposure to the air, gave numbers which rendered it probable that the product consisted of a mixture of magnesium carbonate,  $MgCO_3$ , with the compound  $MgCl^{1.5}MgO.17H^2O$  (a). By drying over sulphuric acid, it was converted into  $MgCl^{1.5}MgO.14H^2O$ ; by drying at  $100^\circ$  into  $MgCl^{1.5}MgO.8H^2O$ ; and at  $150^\circ$ – $180^\circ$  into  $MgCl^{1.5}MgO.6H^2O$ . These facts seem to show that the elements of the chloride and oxide of magnesium have entered into more intimate combination, inasmuch as magnesium hydrate decomposes at  $106^\circ$ . When the above-mentioned sample was treated with water, part of the magnesium chloride dissolved, while (together with magnesium carbonate) the compound  $MgCl^{1.9}MgO.24H^2O$  (b) was formed, from which, by heating to  $100^\circ$  and to  $150^\circ$ – $180^\circ$ , the compounds  $MgCl^{1.9}MgO.16H^2O$  and  $MgCl^{1.9}MgO.10H^2O$  were produced. By prolonged treatment of the compound b with boiling water, the whole of the magnesium chloride could be removed and the residual substance then contained the compound  $2MgO.3H^2O$  (c), from which, by drying at  $150^\circ$ – $180^\circ$ , the compound  $4MgO.5H^2O$  could be obtained.

The compounds a, b, c,  $\gamma$ —if the materials have not been pulverised at the commencement of the process—are compact solid bodies; having the hardness and tenacity of a good sandstone, a brilliant surface, and susceptible of a high polish; their cohesive power is not destroyed by water either cold or hot. In this respect the compound  $\gamma$  resembles the mineral brucite  $Mg(OH)_2$ , the absence of crystallisation being probably due to its rapid mode of formation.

For the proximate constitution of these compounds, C. Bender gives the following formulae:



The compounds dried at  $100^\circ$  and at  $150^\circ$ – $180^\circ$  are similarly constituted. These formulae, however, are not intended to represent the phases of the successive decomposition by cold and hot water, as they would indicate that the compound  $\text{MgCl}^2 \cdot \text{MgO}$  passes in each case into solution, which is not the case.

The crystalline deposit which frequently occurs in the solutions of magnesium salts mixed with sal-ammoniac (known in the laboratory as 'magnesia mixture') consists, according to J. Davis (*Chem. News*, xxv. 258), of the hydrated oxychloride  $\text{MgCl}^2 \cdot 5\text{MgO} + 13\text{H}^2\text{O}$  or  $\text{Mg}^2\text{Cl}^2\text{O} \cdot \text{H}^2\text{O} + 4(\text{MgO} \cdot 3\text{H}^2\text{O})$ . By washing the crystals with a large quantity of water, the whole of the chlorine may be removed, and the oxychloride converted into a hydrated oxide.

**MAGNETISM.** Coulomb's law of the force with which two magnetic poles tend to move towards or away from each other, makes it possible to express the strength of magnetic poles, and the intensity of magnetic forces in general, by reference to the fundamental units employed for the measurement of forces in mechanics. The law itself, which is that the *mutual force* (attraction or repulsion) *acting between two magnetic poles is proportional directly to the product of their strengths and inversely to the square of the distance between them*, leads at once to the following as the definition of a magnetic pole of unit strength: *the unit magnetic pole is such that the force acting between it and another equal pole at the unit distance is unity*. But the effects produced in any actual case by a given magnet do not depend simply on the strength of its poles: for these, being necessarily equal and opposite, neutralise each other's external action the more nearly the smaller the distance which separates them, and it will be shown further on that the resultant force exerted by the two poles of a complete magnet upon each pole of a second magnet is directly proportionate to the distance between the poles of the first magnet as well as to their strength. Hence the true measure of the power of a complete magnet is obtained by multiplying together the strength of its poles and the distance between them. To this product the name *magnetic moment* has been given. In the case of a straight piece of steel, of great length in comparison with its width (such as a piece of thin steel wire), which is uniformly magnetised in the direction of its length, the poles coincide sensibly with the extreme points, so that it would be possible to determine the distance between them by direct measurement. It would also be possible to ascertain approximately the strength of the poles of such a magnet by means of the torsion-balance (MAGNETISM, iii. 758), and so the magnetic moment of the magnet could be calculated from its two factors. But in general, neither the position of the poles of a magnet nor their strength can be determined with anything like accuracy by a direct measurement. It was shown by Coulomb (iii. 760) how the moments of different magnets can be compared, but his method does not give an absolute measure of magnetic moments, since the quantity measured, namely, the moment of the couple required to deflect a magnet through a given angle from the magnetic meridian, depends not only on the properties of the magnet under examination, but also on the intensity of the horizontal component of the earth's magnetic force (iii. 781), which varies with time and place. Hence, in order to be able to determine absolutely the magnetic moment of a magnet, we require either to have some method of measurement which is not affected by the earth's magnetic force, or we must be able to ascertain the intensity of this force. The way in which this can be done was first pointed out by Gauss, in 1832. The phenomena which he employed, as the basis of his system of measurement, were (1) the oscillation of a magnet suspended so as to be free to vibrate in a horizontal plane, in obedience to the magnetic forces exerted upon it by the earth; and (2) the deflection of a declination compass from the magnetic meridian caused by the same magnet, when placed at a known distance from it, with its axis perpendicular to the meridian. From observations of these two phenomena, measures can be obtained respectively of the product of the earth's magnetic intensity into the magnetic moment of the magnet to be examined, and of the ratio of the same quantities; so that a combination of the two sets of observations gives a value of each quantity separately. The general principles of the method are more precisely indicated in what follows.

1. *Determination of the product of the horizontal component of the earth's magnetic intensity into the magnetic moment of an artificial magnet.*

If a magnet is suspended in a horizontal plane by a fibre without sensible torsional rigidity, or on a point without sensible friction, it will be in equilibrium when its axis is in the magnetic meridian; but if displaced very slightly from this position, it will perform isochronous oscillations backwards and forwards from one side of it to the other. The rate of oscillation under such circumstances will depend upon the mass



and dimensions of the magnet, and upon the moment of the couple, which tends to restore the magnet to its position of equilibrium when it is turned from it through an angle of  $90^\circ$ , that is to say, when it is placed at right angles to the magnetic meridian. The moment of this couple is evidently given by multiplying one of the equal but opposite parallel forces, whose points of application are the poles of the magnet, by the distance between their lines of action—that is, by the distance between the poles. Again, these forces themselves depend conjointly upon the magnetic intensity of the earth at the time and place of experiment, and upon the strength of the poles of the magnet; that is, if  $F$  denote the force applied at either pole,  $H$  the horizontal component of the earth's force, and  $m$  the strength of the poles of the magnet, we have—

$$F = Hm;$$

and the moment of the couple due to the forces  $+F$  and  $-F$ , acting at the arm  $l$ , is given by—

$$Fl = Hml = HM,$$

where  $l$  denotes the distance between the poles and  $M$  the magnetic moment of the magnet. The time in which the magnet will make one whole oscillation of very small amplitude may then be represented by—

$$t = 2\pi \sqrt{\frac{i}{HM}},$$

in which  $i$  stands for the 'moment of inertia' of the magnet, or the mass which, placed at unit distance from the axis of suspension, would offer the same resistance to change of angular velocity about this axis that the magnet does.

If the magnet be a rectangular prism of weight  $w$ , and be suspended with two of its faces, whose diagonals measure  $2a$ , horizontal, we have—

$$i = \frac{a^2 w}{3g}.$$

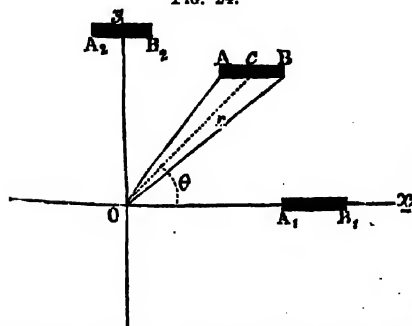
The observations belonging to this part of the process consequently resolve themselves into a determination of the time of oscillation of the magnet and of its moment of inertia. When these are known, the value of the product to be measured is given by the equation—

$$MH = 4\pi^2 \frac{i}{t^2} \quad (1).$$

## 2. Determination of the ratio of the magnetic moment of an artificial magnet to the horizontal component of the earth's magnetic intensity.

In order to explain the principle of this part of the process, it is convenient to consider, first, the action of an indefinitely small magnet upon an isolated magnetic pole

FIG. 24.



in a known position relatively to it. Let  $AB$  be an indefinitely small magnet and let there be at the point  $O$  a magnetic pole of the strength  $m'$ . Then if  $m$  represents the strength of the pole  $A$ , and  $r$  the distance  $AO$ , the force acting between  $A$  and  $O$  will be

$$\frac{mm'}{r^2}.$$

Let  $O$  be taken as the origin of rectangular co-ordinates, the axis of abscissae being taken parallel to  $AB$ . Then the force exerted between  $A$  and  $O$  may be resolved into components  $X'$  and  $Y'$  acting along the axes, which, if  $x$  and  $y$  be the co-ordinates of the point  $A$ , will have respectively the following values, namely—

$$X' = \frac{mm'}{r^3} \frac{x}{r} = \frac{mm'x}{r^4},$$

$$Y' = \frac{mm'}{r^3} \frac{y}{r} = \frac{mm'y}{r^4}.$$

Similarly, the components of the force acting between B and O will be represented by—

$$X'' = -\frac{mm'(x+dx)}{(r+dr)^3}$$

$$Y'' = -\frac{mm'y}{(r+dr)^3},$$

where  $dx$  is the increment of  $x$  in passing from A to B and  $dr$  the corresponding increment of  $r$ . But since  $r^2 = x^2 + y^2$  and  $(r+dr)^2 = (x+dx)^2 + y^2$ , and since also  $dx$  and  $dr$  are indefinitely small, we get  $dr = \frac{x}{r} dx$ ; hence—

$$X'' = -\frac{mm'(x+dx)}{r^3 + 3rx dx} = -\frac{mm'(x+dx)}{r^3} + \frac{3mm'x dx}{r^4},$$

$$Y'' = -\frac{mm'y}{r^3 + 3rx dx} = -\frac{mm'y}{r^3} + \frac{3mm'xy dx}{r^4}.$$

For the resultant forces acting along the two axes we have consequently—

$$X = X' + X'' = -\frac{mm'dx}{r^3} \left(1 - 3 \frac{x^2}{r^2}\right),$$

and

$$Y = Y' + Y'' = \frac{3mm'dx}{r^3} \cdot \frac{x}{r} \cdot \frac{y}{r}.$$

Putting  $\theta$  for the angle AOx, or for what is sensibly the same, namely, COx, we have  $\frac{x}{r} = \cos \theta$  and  $\frac{y}{r} = \sin \theta$ .

Also  $mdx$  is the magnetic moment of the magnet AB, so that, if this be denoted by  $M$ , the above values become—

$$X = -\frac{Mm'}{r^3} (1 - 3 \cos^2 \theta),$$

$$Y = \frac{3Mm'}{r^3} \sin \theta \cos \theta.$$

The total force exerted by the magnet AB upon the pole at O is the resultant of these two; it may be represented by—

$$F = \sqrt{X^2 + Y^2} = \frac{Mm'}{r^3} \sqrt{1 + 3 \cos^2 \theta},$$

and it acts in such a direction that, if  $\phi$  be the angle which it makes with the axis of  $x$ ,—

$$\tan \phi = \frac{Y}{X} = -\frac{3 \sin \theta \cos \theta}{1 - 3 \cos^2 \theta}.$$

From these values it is evident that the component  $Y$  vanishes whenever  $\theta$  is equal either to  $0^\circ$  or to any whole number of right angles. For  $\theta = 0^\circ$  or  $180^\circ$ , we have—

$$F_1 = 2 \frac{Mm'}{r^3}, \quad \phi = 0^\circ.$$

For  $\theta = 90^\circ$  or  $270^\circ$ , we have—

$$F_2 = \frac{Mm'}{r^3}, \quad \phi = 0^\circ.$$

The first of these special cases corresponds with the position  $A_1B_1$  of the magnet, and the second with the position  $A_2B_2$ .

If now, instead of a single magnetic pole, there is at O a magnet whose length  $l$  is an indefinitely small fraction of the distance  $r$ , its two poles will be acted on by equal, but opposite, parallel forces, constituting a couple. When the axis of the magnet at O is parallel to Oy, the moment of the couple tending to place it parallel to Ox is—

$$G_1 = 2 \frac{MM'}{r^3}, \quad \text{for the position } A_1B_1 (\theta = 0^\circ),$$

$$G_2 = \frac{MM'}{r^3}, \quad \text{for the position } A_2B_2 (\theta = 90^\circ);$$

where  $M' = m'l$  is the magnetic moment of the magnet at O.

If, however, the magnet at O is deflected through any angle, say  $\alpha$ , from the direction Oy, the moments of the couples tending to increase the deflection will be obtained by multiplying these values by  $\cos \alpha$ . Further, if Oy be the direction of the earth's magnetic meridian, the magnet at O, when deflected through the angle  $\alpha$ , will be subject to a couple tending to bring it back to the meridian, the moment of which is represented by  $M'H \sin \alpha$ , where H stands for the horizontal component of the earth's magnetism. Consequently, a magnet at O acted upon by the earth, will place itself so that, for every position of the magnet AB, the two couples which act upon it, namely, the couple tending to set it parallel to Ox, and the couple tending to set it parallel to Oy, shall be of equal but opposite moments. For the two special positions of the deflecting magnet already mentioned, the conditions of equilibrium will therefore be represented by the equations—

$$2 \frac{MM'}{r^2} \cos \alpha_1 = M'H \sin \alpha_1 \quad (\text{for the position } A_1B_1),$$

$$\frac{MM'}{r^2} \cos \alpha_2 = M'H \sin \alpha_2 \quad (\text{for the position } A_2B_2).$$

Denoting these two positions, for the sake of shortness, as the *first position* and *second position* respectively, we obtain the two following values of the ratio of M to H, namely:—

$$\frac{1}{2} r^2 \tan \alpha_1 = \frac{M}{H} \quad (\text{for the first position}),$$

$$r^2 \tan \alpha_2 = \frac{M}{H} \quad (\text{for the second position}).$$

These expressions are rigorously true only when the magnets employed are indefinitely small; but they are *nearly* true when the length of the magnets is only a small fraction of  $r$ , the distance between them. The larger they are proportionately to  $r$ , the less nearly is the value of the product  $r^2 \tan \alpha$  constant; but even when the length of the magnets is as much as a quarter of the distance between them, this product can be represented with considerable accuracy by a formula of two terms, of the following form:—

$$r^2 \tan \alpha = A + \frac{B}{r^2}.$$

Here A is evidently the value towards which  $r^2 \tan \alpha$  approximates as  $r$  becomes greater; that is  $A = \frac{M}{H}$  or  $= 2 \frac{M}{H}$ , according as the deflecting magnet is placed in the second or in the first position. It cannot be deduced from any single observation of the deflection of the magnet at O, since the quantity B, which occurs in the same equation, is also unknown. But by observing the deflections corresponding with two different distances of the deflecting magnet, two equations are obtained from which B can be eliminated, and hence the value of A or of the ratio  $\frac{M}{H}$  can be found. Thus, suppose  $\alpha$  and  $\alpha'$  to be the deflections observed when the deflecting magnet is placed in the first position at the distances  $r$  and  $r'$  respectively; the two observations give the equations:—

$$\left. \begin{aligned} r^2 \tan \alpha &= A + \frac{B}{r^2} \\ r'^2 \tan \alpha' &= A + \frac{B}{r'^2} \end{aligned} \right\}$$

whence we obtain—

$$\frac{M}{H} = \frac{1}{2} A = \frac{1}{2} \frac{r^2 \tan \alpha - r'^2 \tan \alpha'}{r^2 - r'^2} \quad (2). \dagger$$

By combining the value of the ratio  $\frac{M}{H}$  thus found with the value of the correspond-

\* Or  $\tan \alpha = \frac{A}{r^2} + \frac{B}{r^4}$ : the fact that when the sign of  $r$  is changed, the *sign* of the deflection, but not its magnitude, is changed also, shows that only *odd* powers of  $r$  can appear in the right-hand member of this equation.

† In practice, the value of  $\alpha$ , corresponding with each value of  $r$ , would be deduced from *four* observations, namely: (1) with the deflecting magnet *east* of the suspended magnet, and with its north pole *east*; (2) deflecting magnet *east*, north pole *west*; (3) deflecting magnet *west*, north pole *west*; (4) deflecting magnet *west*, north pole *east*. In the second position of the deflecting magnet, four corresponding observations would be made; namely, two with this magnet to the north, and two with it to the south of the suspended magnet.

ing product  $MH$  given by equation (1) (p. 761), we obtain the following value for  $M$ , the magnetic moment of the magnet employed:—

$$M = \frac{2\pi}{i} \sqrt{\frac{i}{2} \cdot \frac{r^2 \tan \alpha_1 - r'^2 \tan \alpha_1'}{r^2 - r'^2}};$$

where the magnitudes  $i$ ,  $r$ , and  $i'$ , which appear on the second side of the equation, are all expressible in terms of the fundamental mechanical units of *time*, *space*, and *mass*. The result thus obtained is called the *absolute* value of  $M$ , not in order to signify that it is necessarily very exact, but in contradistinction to the *comparative* value obtained when it is measured by any process which merely enables us to compare one magnet with another, but does not tell us what the actual moment of either of them is.

It is obvious, further, that the same two equations, (1) and (2), afford also a value of  $H$ , or the horizontal component of the earth's magnetic intensity, namely:—

$$H = \frac{2\pi}{i} \sqrt{\frac{2i(r^2 - r'^2)}{r^2 \tan \alpha_1 - r'^2 \tan \alpha_1'}}.$$

The value of  $H$  thus found denotes the force with which a magnetic pole of unit strength would be urged towards the magnetic north or south respectively, or the moment of the couple which would tend to displace a magnet of unit-magnetic moment if it were placed with its axis perpendicular to the magnetic meridian.

(For much of the above see Bertin, *Ann. Ch. Phys.* [4], xix. 483, April, 1870.)

G. C. F.

**MAIZE.** The following table shows the composition of green maize cut for fodder about the time of blossoming; the numbers are the mean of eight analyses. Also the composition of maize-corn, mean of ten analyses of the ripe straw and leaves, and of the empty cobs; the last two are from Knop's *Agricultur-Chemie*, 717:—

	Water	Albumi- noids	Fat	Fibre	Soluble carbo- hydrates	Ash
Green maize . . . .	85.22	1.68	.53	4.41	7.06	1.10
Maize grain . . . .	12.14	10.06	5.01	4.04	67.10	1.65
Straw and leaves . . .	14.00	3.00	1.10	40.00	37.90	4.00
Empty cobs . . . .	14.00	1.40	1.40	37.80	42.60	2.80

Maize-corn is remarkable for the large amount of fat it contains (reaching in some analyses to 9 p.c.) and for its small amount of ash. An analysis of maize-corn by Pillitz's improved method of analysing grain (p. 577) gave: Starch, 62.69; dextrin, .76; sugar, 1.38; fibre, 4.19; soluble albuminoids, 1.87; insoluble albuminoids, 8.63; fat, 4.36; extractive matter, 1.43; soluble ash, 1.15; insoluble ash, .33; water, 13.89 p.c. For earlier analyses see *CHEMICALS*, vol. i. Malted maize contains, according to C. Graham, three times as much soluble albuminoids as malted barley, and is therefore used with advantage when much sugar is used in brewing.

The following is the mean of eight analyses of the ash of maize-corn, with single analyses by Way and Ogston (*Jour. Roy. Agri. Soc.* xi. 497) of the ash of the straw and leaves and of the empty cob:—

	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	Cl	SiO <sup>2</sup>	CO <sup>2</sup>
Maize grain . . . .	27.8	3.9	2.5	15.0	.8	46.8	1.5	trace	1.6	none
Straw and leaves . . .	35.3	1.2	10.5	5.5	2.3	8.1	5.2	1.4	28.0	2.9
Empty cob . . . .	47.1	1.2	3.4	4.1	.2	4.4	1.9	5.1	26.4	7.5

The embryo of the seed has a very different composition from the endosperm. Haberlandt (*Jahrb. Agri. Chem.* 1866, 107) separated the embryo from six varieties of maize; it amounted, on an average, to 11.68 p.c. of the seed. The embryo and endosperm, dried at 60°, contained per cent.:—

	Fat	Albuminoids
Embryo . . . .	30.90	22.77
Endosperm . . . .	1.32	13.34

The whole of the fat seems to exist in the embryo, from which, indeed, oil may be

obtained by treatment with hot water and pressure. The albuminoids of the embryo are soluble, those of the endosperm insoluble.

By extracting maize-flour with spirit of 80–85 p.c. at a temperature of 40°–50°, Ritthausen obtains about 5 p.c. of an albuminoid which he calls maize-fibrin, having the percentage composition—carbon, 54.60; hydrogen, 7.51; nitrogen, 15.58; sulphur, .69; and oxygen, 21.53. It is similar in properties to wheat-fibrin, but is not soluble in dilute acetic acid; the maize-fibrin contains also 1 p.c. less nitrogen. By treatment with  $\frac{1}{2}$  p.c. caustic potash, after the exhaustion with spirit, an albuminoid similar to conglutin is obtained, having the composition: carbon, 51.41; hydrogen, 7.19; nitrogen, 17.72; oxygen and sulphur, 23.68 (*Jour. f. prakt. Chem.* cvi. 471). Garbam's Zein is apparently a mixture of fibrin and casein.

The fat of maize resembles olive-oil; its percentage composition, according to König (*Landw. Versuchs-Stationen*, xiii. 241), is: carbon, 75.79; hydrogen, 11.43; oxygen, 12.78. According to Allemann it contains oleic, stearic, and palmitic acid.

R. W.

**MALDONITE.** This name is applied by G. Ulrich (*Sill. Am. J.* [2], 1. 272) to a native alloy of bismuth and gold occurring in the gold-bearing granito-veins at Nuggety Riff, Malden, Victoria, in small malleable spangles of flesh-red colour, changing to copper-red and black on exposure to the air. Cleavage parallel to  $\infty O\infty$ . Hardness, 1.5 to 2.

**MALEIC ACID,  $C^4H^4O^4$ .** This acid is formed when silver succinate mixed with sand is heated to a temperature somewhat above 108°:  $C^4H^4Ag^2O^4 = Ag^2 + C^4H^4O^4$ . A small quantity of succinic acid is at the same time regenerated and a carbonaceous residue is left. (E. Bourgoïn, *Compt. rend.* lxxii. 52).

To explain the isomerism of maleic and fumaric acids, both of which are converted into succinic acid by addition of hydrogen, it must be assumed either that they are polymerides, or that one of them contains carbon-atoms with free combining units: thus



To decide this question, Hübner a. Schreiber (*Zeitschr. f. Chem.* [2], vii. 712) have determined the vapour-densities of ethyl fumarate and maleic anhydride, both of which can easily be obtained pure, and volatilise without decomposition. That of ethyl fumarate (determined in aniline vapour) was found to be 85.2 to 85.6 ( $H=1$ ); the calculated value for the formula  $C^4H^4(C^2H^3)^2O^4$  being 86; that of maleic anhydride was found to be 47 to 49.13, the calculated value for  $C^4H^4O^4$  being 49. Hence it follows that fumaric and maleic acid have the same molecular weight.

**MALIC ACID,  $C^4H^4O^4$ .** According to Béchamp (*Compt. rend.* lxx. 999) calcium malate fermented with microzyme-chalk (1st Suppl. 614) yields alcohol, acetic, propionic and butyric acids, and free hydrogen.

On *Adipomalic acid,  $C^6H^{10}O^4$* , see p. 29.

On the *Nitrins of Malic Ethers*, see NITRINS.

**MALT.** Malt is prepared by soaking barley in water for about 50 hours. The barley is then thrown on a floor, and allowed to germinate, with frequent turning, until the plumule has reached two-thirds the length of the grain; the radicle is earlier developed and attains a greater length. The malt is then dried in a kiln, and finally screened to remove the radicle and plumule, which constitute malt-dust. 100 parts of barley yield about 80 of kiln-dried malt, and 2 or 3 parts of malt-dust. In the process of soaking about  $\frac{1}{2}$  p.c. of the dry matter of the barley is removed, the loss being chiefly nitrogenous and cinereal matter. In germination a considerable amount of organic matter is lost by oxidation. The total loss in the production of screened malt will be about 10 p.c. of the dry matter of the barley; but if the malt-dust is included in the product, the loss will be about 8 p.c. The loss is of course greater the further germination is allowed to advance. Malt of the same degree of dryness contains less ash, and generally rather less nitrogen than the barley from which it was made, the loss falling most heavily upon these constituents; if, however, the malt-dust is included in the product, the loss chiefly falls on the non-nitrogenous organic matter.

The alteration in general composition during malting is shown in the following table, which gives the percentage composition of the perfectly dry grain in various stages of the process, also the percentage of water in the natural condition. The experiments quoted are taken from the Report of Mr. Lawes to the Board of Trade, 'On the relative Values of Unmalted and Malted Barley as Food for Stock,' 1866.

	Barley	Barley after steeping	4½ days on the floor	8 days on the floor	12½ days on the floor	14½ days on the floor	Screwed Malt	Malt- dust
Sugar . . .	2.66	1.56	8.16	10.10	11.67	12.14	11.01	11.35
Starch, dex- trine, and fat	80.42	81.12	74.72	72.16	70.73	70.09	72.03	43.68
Albuminoids	9.83	9.83	9.89	10.14	10.27	10.39	9.95	26.90
Fibre . . .	4.69	5.22	1.96	5.18	4.98	5.03	4.84	9.67
Ash . . .	2.50	2.27	2.27	2.23	2.35	2.35	2.17	8.40
Water in frosh	17.64	42.70	41.87	41.65	40.71	40.44	6.66	11.73

The determination of sugar in malt is attended with considerable uncertainty; in the above analysis the powdered malt was stirred with cold water for several hours, and the sugar in the solution determined by fermentation and by copper. O'Sullivan informs the writer that alcohol of 91 p.c. extracts 10-12 p.c. of solid matter from malt. This extract chiefly consists of carbo-hydrates, but contains (by the copper test) only about 1.5 of sugar reckoned as dextrose; the sugar is, however, neither dextrose nor maltose, and its nature is not yet established. The cold water extract of malt amounts to 18-30 p.c.; it contains, according to O'Sullivan, both dextrin and maltose, the latter being formed by the action of soluble nitrogenous matter or the gelatinised starch of the malt produced during kiln-drying; ungelatinised starch is not converted into sugar in the cold by extract of malt; the amount of gelatinised starch in malt varies much according to the treatment of the kiln. C. Graham states (*Jour. Soc. Arts*, xxii. 251) that absolute alcohol extracts no sugar from malt, and alcohol of 80 p.c. very little. With alcohol of 80 p.c. 5.68 p.c. of sugar was in our experiment extracted, and nearly the same amount of sugar was removed by 15 minutes extraction with cold water; 30 minutes extraction with cold water gave 7.14 p.c. of sugar. As the sugar was determined by copper, the latter weights should probably be increased (*vide infra*).

Malt contains about 4-7 p.c. of water. In the process of malting the starch has been partially destroyed and converted successively into soluble starch, dextrin, and sugar. Maltin, the soluble albuminoid which effects these changes, has been already described (*1st Suppl.* 801); all soluble albuminoids possess this property to a greater or less extent. When extract of malt acts upon starch-paste the same changes occur, achrodextrin (the dextrin not coloured by iodine) being produced, on which the further action of malt is but slow (Brücke, *Wien. Acad. Ber.* lxx. [3], 126), and the final product is a sugar called maltose (iii. 799). Maltose has been recently shown by O'Sullivan (*Jour. Chem. Soc.* 1872, 579), to be isomeric with cane-sugar; it reduces only 65 p.c. as much cupric oxide as the same weight of glucose; the latter fact explains the opinions hitherto held (founded on experiments with cupric oxide) that two of glucose and one of dextrin were the final products of the action of malt on starch. O'Sullivan confirms the statement of Dubrunfaut that the rotatory power of maltose is nearly three times as great as that of dextrose, being +150. Maltose is readily soluble in 31 p.c. alcohol.

From the great solvent action of malt on starch, it has been suggested that malt would assist the digestion of animals; the trials conducted by Mr. Lawes, referred to above, have shown, however, that with healthy animals the addition of malt to their vegetable food produces a less increase of weight than the addition of the quantity of barley to which the malt is equivalent. From an economical point of view malting is therefore undesirable for feeding purposes.

Malt-dust is used for cattle-feeding; it will vary in composition according to the amount of growth attained; it is remarkably rich in nitrogen and ash constituents. The ash is often contaminated with sand, but the pure ash is not less than 6 p.c. The following is the mean of 11 analyses of malt-dust:

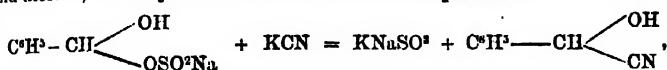
	Water	Albumi- noids	Fat	Fibre	Soluble carbo- hydrates	Ash
Malt-dust . . .	9.52	23.65	2.19	12.51	44.87	7.35

The mean of two analyses of the ash of malt-dust by J. O. Lerner (*Jahrb. Agri. Chem.* 1866, 433) is as follows:

K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	Cl	SiO <sub>2</sub>	CO <sub>2</sub>	Ash p. c.
28.77	2.65	3.54	3.44	.75	1.08	29.92	2.91	7.41	18.36	.91	6.55

Lerner (*see above*) states that he has detected in malt-dust, citric, malic, lactic, propionic, acetic, formic, succinic, oxalic, and tannic acid; also cholesterin and asparagin. R. W.

**MANDELIC ACID, C<sup>8</sup>H<sup>8</sup>O<sup>3</sup>.** This acid, which has the constitution of phenyl-glycolic acid, C<sup>6</sup>H<sup>5</sup>—CH  $\begin{matrix} \text{OH} \\ \text{COOH} \end{matrix}$ , is formed synthetically by boiling the compound of benzoic aldehyde and acid sodium sulphite for several hours with potassium cyanide and alcohol, whereby the nitril of mandelic acid is produced—



then distilling off the alcohol, and decomposing the residual brown mass by boiling with water and hydrochloric acid. The acid liquid is evaporated to dryness, the residue is redissolved in water, and the solution saturated with barium carbonate. On evaporating the resulting solution of barium mandelate to dryness, washing the residue with a mixture of alcohol and ether till it becomes white, and decomposing it with dilute sulphuric acid, a solution is obtained from which mandelic acid may be extracted by ether; it may then be purified by recrystallisation from water (O. Müller, *Deut. Chem. Ges. Ber.* iv. 980).

**MANGANESE ORES.** The Manganese ores of Virginia imbedded in the Potsdam sandstone yield by analysis, after being superficially separated from intimately admixed quartz and micaceous ochre:

Mn <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	H <sub>2</sub> O
65.20	4.75	6.20	3.93	1.43	0.41	0.30	0.42	14.20	3.02 = 99.86.

The micaceous ochre contains:

Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Co <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O	Mica
31.20	1.28	0.23	0.13	5.75	61.18 = 99.77.

The mica contains 34.48 p.c. silica, 20.65 alumina, 2.99 magnesia, and 3.6 potash (J. E. Mills, *American Chemist* [2], ii. 49).

On *Manganese in Iron and Steel*, see *Iron*, p. 601.

**Manganese in Blood.**—Manganese exists in ox-blood, in the corpuscles as well as in the serum, both of which also contain iron. The ash of the corpuscles contains larger quantities of those metals than that of the serum. The portion of the serum-ash which is soluble in water contains traces of iron, but no manganese (G. Campani, *Gazzetta chimica italiana*, i. 469).

**Metallic Manganese.** A. Valenciennes (*Compt. rend.* lxx. 907) prepares this metal by reducing the pure dioxide with charcoal in a crucible lined with magnesia. Manganese thus obtained is very hard and brittle, so that it easily splits under the hammer into fragments, which have the white colour of cast iron, but are quickly oxidised in contact with the air.

The smelting of manganese ores on the manufacturing scale has been studied by Hugo Tamm (*Chem. News*, xxvi. 111), who has succeeded in obtaining refined manganese containing 99.9 p.c. of metal.

The following is an outline of the process:—

**Fluxes.**—Two fluxes are required. No. 1, or white flux, is prepared by mixing together ground glass 63 parts, quicklime 18½ parts, fluor-spar 18½ parts. It is a fusible flux, and is principally required for the preparation of No. 2, or green flux.

The latter is made by smelting together:—Flux No. 1, 34 parts; lamp-black or soot, 5½ parts; manganese dioxide, of good quality, 60½ parts. The slag obtained in this operation alone is required. It presents a fine green colour from the presence of manganates, and when once prepared may be used over and over again, provided the manganese ore reduced is of tolerably good quality. It requires from time to time the addition of a little white flux to increase its fusibility.

**Crucibles.**—On account of the high temperature required for the reduction of manganese, some difficulty was experienced in obtaining a crucible which would withstand the action of the molten flux, but it was finally overcome by lining the crucible with a paste made by mixing 3 parts of plumbago and 1 part of loam or fire-clay with a

small quantity of water. This lining, which should not under any circumstances exceed half an inch in thickness, effectually protects the crucible.

**Smelting the Ore.**—The following proportions are recommended:—

Manganese dioxide, of good quality	1000 parts
Lamp-black or soot, " " "	91 "
Green flux " " "	635 "
Oil in sufficient quantity to wet the mixture.	

The mixture is introduced into a crucible prepared as above directed, and a cover of thick wood placed over it. The wood is carbonised during the smelting, and forms a charcoal cover which protects the mixture from oxidation. A clay cover is subsequently luted over the whole. The crucible is then placed in a wind-furnace, and slowly heated as long as fumes escape; the fire is then urged, and the crucible maintained at a white heat for several hours, the time actually required depending upon the quantity operated on.

When cold, the contents of the crucible are turned out, and the button of metal is detached from the slag, and preserved in a well-closed bottle.

**Refining.**—The cast manganese obtained by smelting an ore containing 79.5 p.c. of manganese peroxide was found to contain manganese 96.9, iron 1.05, with traces of carbon, silicon, and other metals. It may be refined by re-melting it in a close crucible, with one-eighth of its weight of manganese carbonate.

Refined manganese presented the following composition:—

Manganese	Iron	Silicon	Carbon	
99.91	0.05	0.015	0.025	= 100.36.

**Specific Gravity.**—J. E. Loughton (*Chem. News*, xxv. 139) finds that metallic manganese of sp. gr. 7.84 prepared by heating the peroxide made up into balls with charcoal and oil, may be rendered denser by repeated reheating with charcoal, its specific gravity being ultimately raised to 7.903; hence he concludes that the low density of certain specimens prepared by the older methods was due to the presence of oxide. He did not succeed in preparing manganese of sp. gr. 8.015, as obtained by Deville.

**Detection and Estimation of Manganese.** Fresenius (*Zeitschr. anal. Chem.* xi. 113) has examined and compared the various methods used and proposed for the precipitation of manganese from solution. Known quantities of the metal were taken for each experiment, and the weight of the precipitate obtained was checked by determining the quantity left in the mother-liquor and wash-waters.

Guyard's method of throwing down the manganese as dioxide by addition of an excess of potassium permanganate (1st Suppl. 803) gave results considerably too high. W. Gibbs's method of precipitating by oxalic acid in presence of an excess of strong alcohol, and washing with nearly absolute alcohol, gave about 99 p.c. of the manganese present, the rest remaining in solution.

Gibbs's other plan of converting the manganese into phosphate of manganese and ammonium by adding ammonia in excess to the boiling acid solution containing sodium phosphate, and then washing with boiling water, after keeping the whole for about an hour at the boiling point, gave very constant and correct results, especially when cold water was used for washing and the quantity of the wash-water diminished as much as possible by the use of the sucking filter. The phosphate of manganese and ammonium is soluble in 32,092 parts of cold, and in 20,122 parts of boiling water. The precipitate is ignited, and weighed as pyrophosphate.

**Precipitation of Manganous Sulphide.**—The circumstances affecting the accuracy of this method were examined, with the following results:—1. A great excess of ammonia causes the results to come out a little too low. 2. Even a great excess of ammonium sulphide does no harm. 3. Great excess of sal-ammoniac interferes slightly with the precipitation. 4. Yellow ammonium sulphide is at least as good as colourless. The presence of tartaric acid has no effect. 6. Citric acid almost entirely prevents the precipitation of manganous sulphide.

In estimating the small quantities of manganese left in solution, it is customary to drive off the excess of sal-ammoniac by heat, but Fresenius finds that the latter body carries with it a very considerable quantity of manganese.

Hugo Tamm's method of precipitating with ammonium carbonate gives very exact results, very little affected by the presence of sal-ammoniac even in large quantities.

A. Classen (*ibid.* 370), from an examination of the circumstances attending the precipitation of manganese by ammonium sulphide from solutions containing sal-ammoniac and free ammonia, recommends that the ammonium sulphide used for the precipitation should not contain free ammonia, and that the manganese solution should not contain excess of sal-ammoniac or of ammonia.

J. H. Talbut (*Deut. Chem. Ges. Ber.* iv. 279) recommends the precipitation of man-



ganate by ammonium sulphide from a boiling solution containing sal-ammoniac. The precipitate, which is pulverulent and easy to wash, is dissolved in hydrochloric acid, and the manganese estimated as pyrophosphate.

According to E. Prior (*Zeitschr. anal. Chem.* viii. 428) the precipitate formed in solutions of manganous salts, by the neutral and acid carbonates of the alkali-metals, consists of normal manganous carbonate, not of a basic carbonate. Even after the precipitate formed by sodium carbonate has been partially oxidised by exposure to the air, it still (after deduction of the quantity of manganoso-manganic oxide equivalent to the quantity of chloride evolved on heating it with hydrochloric acid) contains 1 mol.  $\text{MnO}$  to 1 mol.  $\text{CO}_2$ .

For How's observations on the influence of fixed organic acids on the precipitation of manganese by ammonium sulphide, see 1st Suppl. p. 803.

T. M. Chatard (*Chem. News* xxiv. 196) has applied Crum's method of testing for manganese with lead dioxide and nitric acid (iii. 606) to the quantitative estimation of small quantities of manganese. He prepared a solution of ammonium oxalate of such a strength that 1 c.c. was equivalent to 0.0005467 gram of manganese. He then weighed out four portions of dolomite, dissolved them in nitric acid, added a little lead dioxide, and boiled, whereupon the red colour of permanganic acid was developed. The solution was passed through an asbestos filter by means of a filter-pump, and then titrated with the solution of ammonium oxalate:

Grams	Cub. cen.	Gram	p.c.
3.1300 dolomite required	39.0	= 0.0216 Mn	= 0.069
2.781 "	33.2	= 0.0181 "	= 0.065
2.0998 "	24.5	= 0.0134 "	= 0.063
1.8671 "	23.5	= 0.0128 "	= 0.062

The method yields good results only when the quantity of manganese present is very small; to large quantities it is not applicable, because it then becomes impossible to convert the whole of the manganese present into permanganic acid, either by means of sulphuric acid, nitric acid, and lead dioxide, or of sulphuric acid and lead dioxide alone.

*On the Estimation of Manganese in Iron and Steel*, see *IRON*, p. 690.

*Valuation of Manganese Dioxide.*—E. F. Teschemacher and J. Denham Smith (*Zeitschr. anal. Chem.* vii. 509) point out that the differences in the results of the valuation of manganese dioxide by different methods arise from the presence of magnetic iron oxide. One of the harder varieties, for example, gave, by Fresenius a. Will's oxalic acid method (iii. 814), 71.5 p.c.  $\text{MnO}_2$ , whereas, by titration with a ferrous salt, it gave only 70.5 p.c.; but, after the iron oxide had been removed by a magnet, the first method gave 72.6, and the second 72.25 p.c. The examination of other samples of manganese dioxide showed that the strength of the magnetic properties of this substance always increases with its hardness; and in the same proportion do the differences in the results of the two methods increase.

E. Scheerer and G. Rumpf (*Zeitschr. anal. Chem.* ix. 46) have subjected the several methods in use for the valuation of manganese dioxide to a comparative examination. The dioxide which served for the experiments was an American sample which, when treated by Fresenius a. Will's method, gave 63.49 to 63.63 p.c.  $\text{MnO}_2$ . Eight experiments were made by dissolving a weighed quantity of harpsichord-wire in hydrochloric acid in a flask filled with carbonic anhydride, introducing the manganese dioxide in a test-tube, and boiling till the reaction was complete; after which the excess of ferrous salt was estimated by titration with potassium chromate. The results varied between 61.39 and 62.54 p.c.  $\text{MnO}$ . In the next place weighed quantities of the dioxide were heated in a flask with fuming hydrochloric acid, and the evolved chlorine was passed into milk of lime. Titration by Penot's method with arsenious acid gave, in seven experiments, results lying between 68.16 and 68.30 p.c. Three experiments made according to Bunsen's iodometric method (the liberated iodine being estimated by Mohr's method with sodium thiosulphate), gave 62.73 to 62.76 p.c.  $\text{MnO}_2$ . It appears, then, that only the first and last methods give results which agree satisfactorily among themselves, and the last alone gives the true commercial value of the sample.

Scheerer a. Rumpf further observe that, in the process depending on the oxidation of ferrous oxide, undecomposed manganese dioxide is often driven to the surface of the liquid, where it cannot act on the ferrous salt. They further regard the use of ferrous salts as unadvisable, on account of the difficulty of keeping them free from ferric oxide and moisture. With reference to the method of absorbing the chlorine by milk of lime, an attempt was made, but without success, to prevent the formation of calcium chlorate, which begins at  $40^\circ$ , by cooling the liquid with Glauber's salt and hydrochloric acid.

Scheerer a. Rumpf finally recommend Bunsen's iodometric method as the most accurate and simple of all. They think, however, that it is not advisable to use less than

half a gram of dioxide in each experiment; and they accordingly bring the resulting solution of iodine in potassium iodide to 250° c.c., and titrate 50 c.c. of this solution. They further point out that it is indisputably necessary to determine the iodine immediately after the evolution of chlorine, since, after a certain time, the results become altered by decomposition of hydriodic acid. The quantities of iodine found after the lapse of 24 hours represented 2 p.c.  $\text{MnO}_2$  more than before.

F. Mohr (*Zeitschr. anal. Chem.* viii. 314) likewise regards the method of distilling the manganese dioxide with hydrochloric acid, receiving the evolved chlorine in solution of potassium iodide, and determining the liberated iodine by titration, as preferable to other methods of estimation, inasmuch as it depends on the evolution of chlorine by the method actually employed in manufacturing operations. He titrates the iodine with a  $\frac{1}{10}$ -solution of sodium thiosulphate.

Fresenius (*Zeitschr. anal. Chem.* ix. 63) recommends that, in performing Bunsen's method of iodometric estimation, the peroxide to be valued should be mixed with magnesite, in order to produce a slow evolution of carbon dioxide, and thereby prevent the potassium iodide solution from being driven back into the generating flask.

E. Luck (*Zeitschr. anal. Chem.* xi. 310) has examined the various disturbing influences that may interfere with the results of Fresenius a. Will's method of manganese analysis. In the analysis of manganese dioxide containing ferrous oxide, by the iron method, and other methods in which the dioxide is directly acted on by hydrochloric acid, the practical value of the sample is at once determined; but in the oxalic acid process of Fresenius a. Will the presence of iron in the sample may cause the value given by the analysis to exceed the actual working value by a number proportional to the fractional amount of the ferrous oxide which, from various circumstances, has escaped further oxidation. Results in accordance with those of other methods may, however, be obtained by adding to the liquid 6 to 8 c.c. of a solution of sodium acetate (1 : 9), inasmuch as, in presence even of small quantities of acetic acid, the ferrous oxide is completely oxidised without the carrying forward of acetic acid vapours by the escaping carbon dioxide. In carrying out the process of Fresenius a. Will it is, however, necessary that the temperature be not allowed to rise above 70°, and that the apparatus, during and after the analysis, be protected from direct sunshine; since, on the one hand, the mutual action of sulphuric acid, oxalic acid, ferric oxide, and a manganoous salt, gives rise at 80°-82° to the evolution of a small quantity of carbon dioxide, and, on the other hand, the formation of carbon dioxide, which takes place under certain circumstances, becomes much more considerable under the influence of direct sunshine.

On circumstances affecting the accuracy of Fresenius a. Will's oxalic method, see also J. Pattinson (*Chem. News*, xxi. 267); E. Scheerer (*ibid.* 284; *Jahresb. f. Chem.* 1870, 991, 992).

**Alloys of Manganese.** Some of these alloys have been examined by F. Fenwick Allen (*Chem. News*, xxii. 194). They cannot well be prepared from metallic manganese, on account of the difficulty of separating the metal from its compounds. To obtain a copper-alloy, a mixture of pure manganic oxide or manganoous carbonate was fused with cupric oxide and charcoal in a plumbago crucible at the highest attainable temperature. The alloy, which was afterwards found disseminated through the mass in granules, fused with moderate facility. An alloy of 75 parts copper and 25 manganese was very hard and brittle while hot, but very elastic and easy to roll when cold. By the addition of zinc, an alloy was obtained resembling the inferior sorts of nickel-silver, and easy to work either hot or cold. The experiments were repeated with similar results in a crucible capable of containing 100 pounds of metal. An alloy containing from 5 to 30 p.c. manganese was more malleable, ductile, and tough than copper. Mixed alloys of manganese with tin, lead, and other metals, are well adapted for the journals of machinery. Such alloys cannot be prepared on the large scale in plumbago-crucibles, as too much manganese passes into the slag, and the wear of the crucible is very considerable. They are best prepared in a Siemens' furnace with reducing flame.

A. R. v. Schrötter (*Wien. Akad. Ber.* [2te. Abth.] lxxiii. 451) states that the method of preparing manganese alloys on the large scale was discovered in 1849 by the late Hofrath R. v. Gersdorff. Schrötter himself also prepared an alloy of manganese and copper by igniting manganoous-manganic oxide with cupric oxide and charcoal, and, in like manner, an alloy of manganese, copper, and zinc.

Respecting the alloys of manganese and iron (ferromanganese, spiegelmaess), and their use in the manufacture of steel, see IRON (p. 699).

**Manganoous Chloride,  $\text{MnCl}_2$ .** According to Knecks (*J. pr. Chem.* [2] v. 195) this salt exhibits remarkable changes of colour when its aqueous solution is evaporated to certain degrees of concentration. On concentrating it at a temperature between

70° and 100°, the solution, which is at first colourless, becomes rose-coloured, afterwards yellow, and finally, before crystallising, a splendid green. A solution of rose-coloured crystals of manganous chloride in 10 to 12 parts of water is colourless, either cold or boiling. On evaporating on the water-bath, a little over 70°, and strongly concentrating, the rose colour is developed and gradually increases in intensity, the maximum tint being attained when the solution contains about 15 p.c. of the salt. On further concentration the rose-tint passes into orange, and at last, when the strength of 20 p.c. is attained, the colour becomes a clear yellow, like that of a solution of potassium chromate. On cooling below 70° the rose-tint is regained. Crystallised manganous chloride, dried at 100°, forms a clear green mass, not hygroscopic like the original salt. This mass dissolves partially in water, with liberation of heat, yielding a red solution. The undissolved portion is a white pulverulent basic salt, soluble in dilute acid (Krecks).

According to K. J. Bayer, on the contrary (*ibid.* 445), perfectly pure manganous chloride does not exhibit these remarkable changes of colour; but if small quantities of ferric chloride or cobaltous chloride be previously added to the manganous solution, the changes of colour make their appearance during evaporation exactly in the manner described by Krecks. In the case of cobalt chloride the colour is so characteristic that it may serve very well for the detection of small quantities of cobalt in a concentrated solution of manganous chloride.

Bayer remarks, also, that pure anhydrous manganous chloride is not green, but an easily fusible red body, which solidifies, on cooling, to a beautiful crystalline mass, having a lustre like that of magnesium chloride.

**Oxides.** The oxides  $MnO^2$  and  $Mn^2O^4$  are reduced to manganous oxide,  $MnO$ , by carbon monoxide at the temperature of melting zinc;  $MnO^2$  suffers the same reduction even at a heat just below redness (L. Boll, *Chem. News*, xxiii. 258).

Pure manganous oxide may be prepared as follows:—A solution of potassium permanganate saturated at 60°, filtered through paper free from lime, is added to a saturated oxalic acid solution, and the liquid is decomposed with acetic acid and boiled. The precipitate is repeatedly washed with water by subsidence and decantation, dried in a platinum basin, ignited and reduced in a stream of pure dry hydrogen. Thus prepared, manganous oxide has a light green colour, the solution in dilute hydrochloric acid being slightly brown (F. Kessler, *J. pr. Chem.* [2], vi. 172).

Pyrolusite,  $MnO^2$ , from Giessen, contains, according to an analysis by E. Stapf (*Arch. Pharm.* [2], cxliii. 194):—

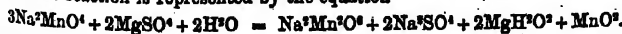
MnO <sup>2</sup>	FeO <sup>2</sup>	AlO <sup>2</sup>	CaO	BaO	MgO	CoO	
94.32	1.98	0.66	1.97	0.43	0.065	trace	= 99.425.

**Manganates and Permanganates.** The preparation of a number of these salts on the large scale is described by E. Desclabissac (*Dingl. pol. J. cci.* 58). a. 500 lbs. of potash-ley (45° B.) and 100 lbs. potassium chlorate are evaporated down in an iron pot, 182 lbs. of finely pounded manganese dioxide are added, and the mixture is heated till it fuses quietly. The mass, after being stirred till it is cold, is heated to redness in iron pots, and after again cooling is boiled out with water.

b. A solution of 12 parts sodium hydrate (36 parts soda-ley of sp. gr. 1.337 and 34 parts soda-ley of sp. gr. 1.365) is fused with 12 parts potassium chlorate and 18 parts manganese dioxide till the mass begins to crumble. The mixture is then heated to redness in an iron melting-pot, and after cooling exhausted with 200 to 220 parts of hot water.

c. Ten parts of caustic soda and 1 part potassium nitrate are fused together, and 6 parts of strongly heated manganese dioxide are thrown into the quietly fusing mass. The fused mass in the crucible, as soon as it dissolves as completely as possible in water with a deep green colour, is ladled out, and the crucible immediately recharged. The muddy deposit which remains in the pot when the melted mass is dissolved in water, is lixiviated with water, and this water is utilised for dissolving a new melt; or chlorine is passed into the aqueous solution, and the resulting liquid is used as a disinfectant.

d. Tessié du Mothay and Maréchal work up the fused mass of sodium manganate—which they obtain by melting the residues of chlorine preparations with caustic soda in contact with the air—to sodium permanganate, by treating it with magnesium sulphate. The reaction is represented by the equation—



With reference to this process, Desclabissac observes that contact of air is essential to the formation of good oxidation-products, the oxidising salts alone not being sufficient for the purpose. Manganese dioxide and sodium nitrate heated together to redness for a considerable time in the muffle of a stone-ware furnace, and lixiviated with hot water

after cooling, yield a solution which on cooling deposits nearly colourless crystals having the composition  $\text{Na}^+\text{MnO}_4^- + 10\text{H}_2\text{O}$ . These crystals in dissolving in water are partly decomposed and acquire a green colour.

**Decomposition of Potassium Permanganate by Sulphuric Acid.**—Spieß (*J. pr. Chem.* [2], i. 421) observes that when pure sulphuric acid is poured upon this salt in the state of powder, violet vapours are evolved which condense in the neck of the flask to a brown-black sublimate, which turns brown when treated with water and yields a solution containing sulphuric acid and manganous oxide, but no potash. Heated with strong sulphuric acid it gives off gas, and yields a dark violet solution, which when diffused in water assumes the colour of a manganous salt. Kolbe (*ibid.* 423) is of opinion that the sublimate obtained by Spieß was probably nothing but permanganic acid containing a little sulphuric acid. He remarks also that Unverdorben (*Pogg. Ann.* vii. 322), by distilling potassium permanganate with sulphuric acid, obtained a red transparent gas which was quickly resolved into manganic oxide and oxygen (*vide* PERMANGANIC ACID, iii. 819).

**Action of Reducing Agents.**—According to Aschoff (*J. per. Chem.* lxxxi. 20 : *Jahresb.* 1860, 167) a neutral solution of potassium permanganate is coloured green by addition of caustic potash. Mohr, however (*Zeitschr. anal. Chem.* ix. 43), has shown that this effect is produced only when the caustic alkali contains organic matter. A solution of the permanganate mixed with previously fused caustic soda may be heated to boiling without turning green. An alkaline solution of permanganate affords indeed an extremely delicate test for the presence of organic matter and of reducing substances in general. Sugar, gum, paper, starch, and other organic bodies which do not act readily on permanganic acid in acid solution, instantly turn it green in presence of excess of alkali. The alkaline solution of permanganate is also a very delicate test for thiosulphates (see further *Jahresb. f. Chem.* 1870, 333, 995).

**Manganous Sulphide.** According to F. Muck (*Zeitschr. f. Chem.* vi. 6) flesh-coloured manganous sulphide is not altered by heating to  $140^\circ\text{--}150^\circ$  for four or five hours in a sealed tube with water, hydrogen sulphide, and ammonia; yellow ammonium sulphide under the same circumstances completely converts it into green manganese sulphide; potassium polysulphide forms a closely adhering violet precipitate, but leaves the manganous sulphide otherwise unaltered; caustic potash decomposes it, with formation of greyish-white manganous hydrate. Under ordinary pressure, water, ammonia and potassium polysulphide do not act upon manganous sulphide; when treated with a very large quantity of ammonium sulphide it turns green, but it is not acted on by a small quantity of that reagent, and not even when first warmed with a small quantity of it and then mixed with a large excess. Potash-ley decomposes manganous sulphide even in the cold, more quickly on warming, the sulphide not being reproduced; on the other hand, recently prepared manganous hydrate is but slowly converted into manganous sulphide by sodium sulphide, though easily by ammonium sulphides.

A. Wagner (*Dingl. pol. J.* xcxy. 532) has examined the behaviour of hydrogen sulphide towards manganese compounds, and the regenerability of manganese sulphide, with reference to the use of manganese compounds for the purification of coal gas from hydrogen sulphide. A stream of hydrogen sulphide was passed for six hours over air-dried manganous hydrate, whereupon the mass became very hot, and the product was exposed for a week to the action of the air. It was then found to contain 34.4 p.c.  $\text{Mn}^2\text{O}^3$ , 32.2 MnS, 1.5  $\text{MnSO}_4$ , 23 p.c. sulphur soluble in carbon sulphide, and 8.2 water. Hence it appears that a week is not sufficient for the regeneration of the manganous sulphide. Moist carbon dioxide expels hydrogen sulphide from manganese sulphide; hydrogen sulphide, on the contrary, acts but very slowly on manganous carbonate. Manganese dioxide tolerably free from iron decomposed hydrogen sulphide completely; after the mass had been exposed to the air for a week, it gave off only traces of hydrogen sulphide when treated with hydrochloric acid, and then contained only 6.1 p.c. free sulphur to 33.1 p.c. manganese; only traces of the sulphur had been oxidised to sulphuric acid. Manganese dioxide, which had been treated with hydrogen sulphide, gave off that gas when carbon dioxide was passed over it, and contained, after regeneration, 5.0 p.c. sulphur to 29.9 p.c. Mn.

**MANGANESE SPAR,  $\text{MnCO}_3$ .** (1.) A highly calcareous variety of this mineral, rose-coloured, and of sp. gr. 3.032, occurring with willemite at Minehill, Sussex Co., New Jersey, has been analysed by W. T. Roepper (*Sill. Am. J.* [3], i. 37); (2.) Manganese-spar from Dietz in Nassau, forming a flesh-coloured nodular coating on clay-slate, by Höhn a. Enders (*Arch. Pharm.* [2], cxliii. 198)—

MnCO <sup>2</sup>	CaCO <sup>2</sup>	FeCO <sup>2</sup>	MgCO <sup>2</sup>	CoCO <sup>2</sup>	Insoluble	
43.64	50.40	0.76	6.69	—	0.08	= 100.47
90.88	1.96	5.85	0.41	0.91	—	= 100

**MANGANITE**,  $H^2(Mn^2)O^4$ . On the isomorphism of this mineral with chrysoberyl, diaspore, and gôthite, see p. 572.

**MANNITE**,  $C^6H^{14}O^8$ . *Formation*.—Linnemann (*Ann. Ch. Pharm.* cxxiii. 136) found that invert-sugar is converted by nascent hydrogen (water and sodium amalgam) into mannite. Dewar (*Phil. Mag.* [4], xxxix. 345) confirms this statement, but considers that there is no ground for supposing that lavulose is the only kind of sugar that can be converted into mannite by addition of hydrogen. In no case is the conversion of the sugar into mannite complete, a gummy uncrystallisable substance being always formed at the same time. Glucose from honey also yields mannite when treated as above. Milk-sugar does not appear to be converted into dulcitol under similar circumstances.

*Optical Rotatory Power*.—Mannite has hitherto been classed among substances inactive to polarised light: for though many of its substitution-derivatives rotate the plane of polarisation, this power had not been directly demonstrated for mannite itself. Recently, however, L. Vignon (*Ann. Chim. Phys.* [6], ii. 433; *Compt. rend.* lxxvii. 1191) has established the existence of this power in mannite, by mixing its saturated solution with boric acid or borax, and examining the action of the resulting liquid on polarised light. Boric acid indeed is known, from the researches of Biot and Pasteur, to possess the singular property of augmenting the rotatory power of tartaric and malic acids; and Vignon finds that it likewise increases the optical activity of mannite to such an extent that a dextrorotatory action can be clearly perceived, a mixture of the saturated solutions of mannite and boric acid producing in a Soleil's apparatus, with a tube 200 mm. long, a deviation of about 5 degrees.

On evaporating this solution over the water-bath, a viscid mass is obtained, which when treated with absolute alcohol, gradually changes to a white powder consisting of mannite, again appearing inactive to polarised light, and the boric acid is found in the alcoholic solution, with all its usual properties. It appears, therefore, that the boric acid has not entered into chemical combination with the mannite. On adding crystals of sodium carbonate to the mannite-boric solution, the salt dissolves with effervescence and the dextrorotation increases to 20 degrees. A similar result is obtained on adding borax to a saturated solution of mannite.

These facts show that mannite possesses rotatory power. The boric acid and borax do not combine with it, but merely increase, by an action which is peculiar to them, the dissymetry which pre-existed in the molecules of the mannite. It may, therefore, also be inferred that the rotatory power exhibited by the ethers of mannite, pre-exists in the mannite itself, and is not created by the act of etherification.

Arsenic acid and its salts likewise increase the rotatory power of mannite, the increase being progressive when the mixture is left to itself. Thus a mixture of mannite and arsenic acid which, immediately after solution, gave for the yellow ray in a tube 200 mm. long,  $\alpha_D = + 0.3924^\circ$ , gave after 24 hours  $\alpha_D = + 1.090^\circ$ ; and a mixture of mannite with potassium diarsenate exhibited the following variations of rotatory power—

Immediately after solution	$\alpha_D = - 5.25^\circ$
After 24 hours	$\alpha_D = - 10.1783^\circ$
" 4 days	$\alpha_D = - 10.82^\circ$
" 6 days	$\alpha_D = - 10.82^\circ$

Pastour (*Compt. rend.* lxxvii. 1192) reports that Bichat, by operating with a tube 4 meters long, has obtained a direct demonstration of the rotatory power of mannite in aqueous solution.

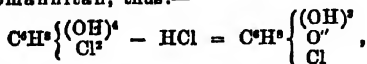
*Action of Water on Mannite at Different Temperatures*.—Mannite, heated with water in sealed tubes for three hours, undergoes no alteration below  $280^\circ$ ; but at that temperature it is converted into a viscid product which, when purified in the manner to be presently described, has the composition of mannitic ether,  $C^{12}H^{20}O^{11}$ . The viscid product gradually deposits a small quantity of a crystalline body which pre-existed in the mixture; it is isomeric with mannitan, and is called, for distinction, mannitone.

Mannite, heated with water to  $287^\circ$ , no longer yields mannitone, but only mannitan, mannitic ether, and a small quantity of unaltered mannite.

Lastly, mannite, mannitone, and mannitic ether, heated, together or separately, with water to  $295^\circ$ , are completely transformed into mannitan (Vignon).

**Chloro- and Bromo-Derivatives of Mannite** (G. Bouchardat, *Compt. rend.* lxxiv. 1187; lxxvi. 1550; *Bull. Soc. Chim.* [2], xix. 199).

**Dichloromannite**,  $C^6H^8(OH)Cl^2$ , is prepared by heating 1 part of mannite with 6 parts of strong hydrochloric acid to  $100^\circ$  in a sealed tube for 6–10 hours. The product, dried over quick-lime and oil of vitriol for about a month, yields light yellow scales which, when dissolved in cold water and recrystallised, yield dichloromannite in monoclinic crystals soluble in 22 parts of water at  $14^\circ$ . This compound is laevogyrate, its molecular rotatory power for the yellow ray being  $-3.7^\circ$ . The aqueous solution is neutral and tasteless, and is not precipitated by silver nitrate. Dichloromannite is insoluble in absolute alcohol and in ether. It melts at  $174^\circ$ , being at the same time decomposed; at a higher temperature it volatilises completely. Its vapour burns with a green-edged flame. Boiling water, or concentrated solution of alkali, rapidly converts it into monochloromannitan, thus:—



just as dichlorhydrin is converted into epichlorhydrin.

Nitrosulphuric acid converts dichloromannite into dichloro-tetranitromannite,  $C^6H^8 \left\{ \begin{matrix} (NO^2)^4 \\ Cl^2 \end{matrix} \right\}$ , which is insoluble in water, but soluble in boiling alcohol, separating from that solution, on cooling, in fine needles. This substance is not easily explosive, notwithstanding its composition; it is, in fact, more stable than dichloromannite. It melts at  $145^\circ$ .

**Dibromomannite**,  $C^6H^8 \left\{ \begin{matrix} (OH)^4 \\ Br^2 \end{matrix} \right\}$ , is prepared in a similar way to the analogous chlorine-compound, the mannite and hydrobromic acid being heated together for two hours only. Crystals appear after a considerable length of time, and are purified by rapid solution in hot water and cooling. Dibromomannite is tasteless, scentless, insoluble in cold water, alcohol, and ether, but soluble in warm water, and in concentrated hydrobromic acid. It crystallises in small colourless plates, melting, with decomposition, at  $178^\circ$ .

Nitrosulphuric acid converts dibromomannite into dibromo-tetranitromannito,  $C^6H^8 \left\{ \begin{matrix} (NO^2)^4 \\ Br^2 \end{matrix} \right\}$ , which crystallises in long needles, insoluble in water and in cold alcohol, but soluble in the latter when it is heated.

The compounds above described are isomeric with the dulcitol-ethers (p. 441); they give similar reactions, with one exception, viz., that when treated with alkaline hydrates, the mannitic ethers furnish mannitan, whereas those of the dulcitol series yield dulcitan, which may be recognised by converting it into mucic acid (Bouchardat).

**Aceto-mannites** (Schützenberger, *Ann. Ch. Pharm.* clx. 74).—Mannite, heated in an open vessel with acetic anhydride containing 10–15 p.c. of acid, dissolves, and the product, on cooling, becomes a mass of indistinctly-shaped crystals which, after separation of syrupy mother-liquor by filtration through asbestos by means of a filter-pump, and washing with alcohol, forms a solid, white, very light substance, apparently homogeneous, scarcely soluble in boiling alcohol, soluble in water and acetic acid, insoluble in ether: it has a faint, sweet and bitter taste, and is feebly dextrorotatory; its composition is that of a monacetyl derivative of di-mannitic anhydride,  $C^{12}H^{22}O^{10}$ , viz.,  $C^{12}H^{22}(C^2H^3O)O^{10}$ . On saponification, this body yields a faintly sweet substance apparently identical with mannitan.

By the further action of acetic anhydride a thick syrup is obtained which, on treatment with water, gives a precipitate crystallisable from boiling water or alcohol; this is **hexaceto-mannite**,  $C^6H^8(C^2H^3O)^6O^6$ ; it melts at  $100^\circ$ , and becomes crystalline on cooling. It has no action on polarised light. [According to Bouchardat it has a dextrorotatory power,  $[\alpha]_D = +18^\circ$ .] The syrupy mother liquors of this compound give on evaporation an extremely bitter substance easily soluble in water, acetic acid, and alcohol; it is dextrorotatory,  $[\alpha] = 22.6^\circ$ ; has the composition  $C^6H^{16}(C^2H^3O)^6O^6$ , and appears to be identical with diacetomannitan (compare *1st Suppl.* 808).

**MANNITIC ANHYDRIDES.** 1. **Mannitic Ether**,  $C^{12}H^{22}O^{11} = \frac{(C^6H^8)^2}{H^2} O^{11}$ .

—This compound, the first anhydride of mannite, is formed, as above stated (p. 773), by heating mannite with water to  $280^\circ$  for three hours. On dissolving the product in water, filtering, evaporating to dryness, dissolving the residue in absolute alcohol, filtering, and again evaporating, a viscid substance is obtained which, after a while, deposits crystals. These may be separated from time to time by means of absolute alcohol, which dissolves the viscid substance and leaves the crystals; after about a

month they cease to form. The viscid mass is then redissolved in absolute alcohol; the liquid evaporated; the residue boiled for an instant with water; the resulting solution filtered through animal charcoal and evaporated to dryness; the residue washed with ether, and redissolved in absolute alcohol; the filtered solution once more evaporated to dryness; and the residue dried at  $120^{\circ}$  till it no longer loses weight.

Mannitic ether thus obtained is a slightly yellowish mass, having the consistence of turpentine, a bitter-sweet taste, very soluble in water and alcohol, insoluble in ether. It is levogyrate;  $[\alpha]_D = -5.59^{\circ}$ . It does not reduce potassio-cupric solution or ferment with yeast. It is not converted into mannite or mannitan by boiling for six hours with dilute sulphuric acid or baryta-water. It unites with strong sulphuric acid, forming a sulphonic acid identical with that obtained from mannitan. With a mixture of sulphuric and nitric acids it forms a nitro-derivative analogous to nitro-mannitan. Heated with water in a sealed tube for two hours it is completely transformed into mannitan.

All these reactions show that the compound in question is a true ether of mannite.

2. *Mannitan*,  $C^*H^{12}O^5 = C^*H^{11}O^5 - H^2O$ .—This compound was discovered by Bertholot, who obtained it by boiling mannite with hydrochloric acid, and by the saponification of mannitic ethers (iii. 825). Vignon (*Ann. Chim. Phys.* [5], ii. 458) prepares it by mixing pulverised mannite with half its weight of strong sulphuric acid, gradually heating the mixture, with constant stirring, to  $125^{\circ}$ , at which temperature it must be kept stationary. After about two hours the mixture is gradually saturated with barium carbonate, without allowing the temperature to fall, as otherwise too much sulphomannitic acid would be formed. After complete neutralisation the mass is left to cool and exhausted with absolute alcohol, the solution is filtered and evaporated over the water-bath, and the residue dried at  $120^{\circ}$ .

The viscid product thus obtained is mannitan. Its formation is due to direct dehydration of the mannite, not to the previous formation of sulphomannitic acid and its subsequent decomposition into sulphuric acid and mannitan. This is shown by the following facts. If barium sulphomannitate, prepared by heating 1 mol. mannite with 1 mol. sulphuric acid to  $100^{\circ}$ , saturating with barium carbonate, filtering, and evaporating, be heated to  $125^{\circ}$  for two or three hours, it quickly acquires an acid reaction, and, if the mass be then saturated with barium carbonate, it yields barium sulphate and mannitan; but if the sulphomannitate be heated to the same temperature, after being mixed with excess of barium carbonate, so that the mixture remains constantly neutral, the sulphuric acid being neutralised as fast as it is set free, no mannitan is formed, the only products obtained being barium sulphate and mannite. It is clear, then, that the production of mannitan in the former case arose from the action of the free sulphuric acid on the mannite resulting from the decomposition of the sulphomannitate. It may therefore be concluded that the formation of mannitan from mannite by the action of sulphuric acid is an act of simple dehydration.

Mannitan is a very viscous substance, having a saccharine, slightly caramelic taste; very soluble in water and in absolute alcohol, insoluble in ether. Its molecular rotatory power is  $[\alpha]_D = +36.6^{\circ}$ . It does not reduce potassio-cupric tartrate or ferment in contact with yeast. It deliquesces when exposed to the air, but is not converted into mannite even in the course of a month. Neither does it yield any perceptible quantity of mannite when heated for some hours with dilute sulphuric acid or baryta-water. When treated with a mixture of strong sulphuric and fuming nitric acid, it is converted into nitromannitan. Heated with oxalic acid, it reacts like a polyatomic alcohol, producing formic acid and carbon dioxide. It unites with sulphuric acid, forming a conjugate acid, the barium salt of which is uncrystallisable, easily decomposable, especially when heated, and very soluble in water.

*Nitromannitan* is prepared by gradually adding 1 part of mannitan to a mixture of 10 parts strong sulphuric acid and  $\frac{1}{2}$  parts fuming nitric acid, keeping the mixture cool for a quarter of an hour, then pouring it into water, whereupon a copious white precipitate is formed, and a brownish-yellow liquid resembling melted phosphorus gradually falls to the bottom. This liquid is washed with water and digested with ether, which dissolves the nitromannitan, and the solution is evaporated at the ordinary temperature and further concentrated in a vacuum.

Nitromannitan is insoluble in water, but soluble in alcohol and in ether. When dissolved in a mixture of alcohol and ether it has a molecular rotatory power  $[\alpha]_D = -52.26^{\circ}$ .

When heated it gives off nitrous vapours and an odour like that of ethyl nitrate; then at a higher temperature the mass swells up and quickly takes fire, leaving a carbonaceous residue. It detonates violently under the hammer. Ammonium sulphhydrate easily reconverts it into mannitan having the same rotatory power as the original substance.

The physical characters and detonating properties of nitromannitan render it diffi-





ammonia and nitric acid than rain collected in country places; also that light showers are far more nitrogenous than long-continued heavy rain.

Agricultural statistics plainly show that more nitrogen is obtained from the atmosphere in an ordinary rotation than is on an average supplied by rain. If we take any well-established rotation, on soil not deficient in cinereal plant-food, and compare the amount of nitrogen in the crops with that supplied in the manure, we are forced to this conclusion. Whether this nitrogen is obtained from the air by the crops or by the soil, or if by crops, by which crops, are questions that are as yet very imperfectly answered.

The amount of ammonia in the atmosphere is, according to Ville, about 1 part in 50,000,000. In Boussingault's experiments, plants protected from rain, but allowed free access of air, assimilated only a very small quantity of nitrogen, the trace of ammonia in the air having no practical effect. Sachs, and latterly A. Mayer (*Deut. Chem. Ges. Ber.* vi. 1410), and T. Schlössing (*Compt. rend.* lxxviii. 1700), have grown plants in an atmosphere artificially enriched with ammonia; under these circumstances nitrogen was assimilated by the plant, but even then not to an extent sufficient for normal growth. The direct effect of the combined nitrogen of the atmosphere on the nourishment of crops is probably therefore but small. The question whether plants can assimilate the free nitrogen of the atmosphere has been already referred to (iii. 828).

Various chemists hold that the soil obtains nitrogen from the atmosphere. Ammonia is possibly absorbed in small quantity by the humus, clay, and ferric oxide of the soil. It has also been argued that the oxidation of organic matter in the soil must be attended with the formation of ozone, which, acting on the nitrogen of the air, may produce nitric acid. Boussingault has, however, lately shown (*Compt. rend.* lxxvi. 22) that nitrification in a vegetable soil is attended with a loss and not a gain of nitrogen. Lastly, P. Déhérain has shown (*Bull. Soc. Chim.* [2], xix. 538) that a mixture of glucose and caustic alkali exposed to pure nitrogen for some time may absorb a portion of the gas even in the cold, and the absorption becomes distinct if the temperature is raised; results less marked were obtained with moist sawdust. He thinks that ammonia is first produced, and then forms compounds similar to the *glucose azoté* of P. Thénard; no proof of the formation of ammonia is given. Déhérain concludes that in the lower layers of the soil, where little oxygen is present, the decomposing vegetable matter absorbs nitrogen and thus enriches the soil.

Against these possible accumulations of nitrogen by the soil and plant has to be placed the well-ascertained loss of nitric acid in drainage-water, with other possible sources of loss to be considered presently.

The conditions which affect the agricultural statics of nitrogen are thus both complicated and obscure. One set of facts—namely, the amount of nitrogen obtainable in the form of crops from land receiving no nitrogenous manure—is being gradually ascertained at Rothamsted. Mr. Lawes has kindly furnished the writer with the following figures, which represent approximately the amount of nitrogen, in pounds per acre, contained in crops growing continuously on the same land without nitrogenous manure. In the rotation experiment the crops consist of turnips, barley, beans or clover, and wheat. The whole of the crops are removed from the land.

*Nitrogen removed in Crops grown without Nitrogenous Manure.*

Nature of Crop and Manure	Average Nitrogen removed in crop per acre per annum
	lbs.
Wheat, 20 years } without manure, and with purely cinereal } Barley " } manure . . . . . }	20-25
Oats, 4 years, without manure, and with purely cinereal manure	18-23
Beans, 21 crops, without manure . . . . .	about 30
" " with purely cinereal manure . . . . .	" 45
Meadow-grass, 18 years, without manure . . . . .	" 36
" " with purely cinereal manure . . . . .	" 56
Rotation, 20 years, without manure . . . . .	30-35
" " with superphosphate to turnips only . . . . .	35-40

The above figures must be taken as simply representing the present state of the experiments. In some cases the crops are slowly falling off, showing that a part of the nitrogen in the crop has been obtained from past accumulations in the soil; in

other cases we have yet to learn whether the crops diminish, before we can safely conclude that the whole amount of nitrogen in the produce is obtained from the atmosphere. The figures show that leguminous crops yield far more nitrogen than graminaceous crops, even when nitrogenous manure has been for many years withheld. The mixed herbage of meadow-grass stands much higher than the cereals as to the amount of nitrogen harvested each year, and where cinereal manures are applied to the meadow the nitrogen annually removed in the crop reaches the maximum point in the table. In the latter case the manure has developed a very considerable growth of clover, which accounts in great measure for the high nitrogen obtained. This most interesting plot as yet shows no signs of falling off in its produce.

The production of clover on meadow-land by cinereal manures containing potash is of considerable interest. In 1856, at the commencement of the grass experiments at Rothamsted, the herbage appeared uniform upon all the plots; various manuring has, however, strikingly changed the character of the herbage. A series of botanical analyses of the hay has been made, the first only of which has been hitherto published (*Jour. Roy. Agri. Soc.* 1863); the following summary of the results for four of the principal plots has been kindly communicated by Messrs. Lawes and Gilbert.

*Percentage Botanical Composition of Meadow-Hay variously Manured.*

Manuring	1862			1867			1872		
	Gram- inaceæ	Legum- inoseæ	Other orders	Gram- inaceæ	Legum- inoseæ	Other orders	Gram- inaceæ	Legum- inoseæ	Other orders
No manure	71.52	7.15	21.33	62.27	8.07	29.66	66.18	9.58	24.24
Mixed cinereals	64.65	24.70	10.65	59.29	12.60	28.02	48.82	39.77	11.41
Ammonium salts	86.32	.12	13.56	71.85	.34	27.81	84.70	.46	14.84
Mixed cinereals and ammonium salts	88.59	.13	11.28	77.06	.16	22.78	92.19	.02	7.79

The cinereal manure supplies lime, magnesia, soda, phosphoric and sulphuric acids, besides potash; but where the potash only is omitted, the characteristic growth of clover ceases. It is seen that ammonia prevents the growth of clover even when potash is present.

In ordinary agriculture, as is well known, a great part of the constituents of the crops are returned to the land in the form of farmyard-manure, while the remainder is lost by sales of produce. The average loss of ash-constituents, in an ordinary rotation, by the sale of corn and meat, has been already given in detail (see previous article on MANURE, iii. 832-842). To complete the subject we proceed to consider the chemistry of farmyard-manure.

Farmyard-manure consists of the solid and liquid excrements of the stock of the farm, *plus* the straw used as litter. The value of the manure will depend greatly on the character of the animals contributing to it. In the case of a working animal, as a horse or draught-ox, the whole of the nitrogen and ash-constituents contained in the food will appear in the manure. In the case of fattening animals, or of animals producing milk or wool, a part of the nitrogen and ash-constituents of the food will be retained by the animal, and the manure will be of poorer quality. The quantity of nitrogen and ash-constituents contained in the various animal products of a farm, and consequently not recovered in the manure, will be gathered from the following table. The composition of the fat ox, sheep, and pig is deduced from the experiments at Rothamsted, in which whole bodies of animals were submitted to analysis.

*Composition of the Animal Exports from a Farm.*

	Nitrogen	Phosphoric acid	Potash	Lime	Magnesia
	lbs.	lbs.	lbs.	lbs.	lbs.
Fat ox, 1,000 lbs. fasted live } weight	23.18	16.52	1.84	19.20	.63
Fat sheep, 1,000 lbs. fasted live } weight	19.60	11.20	1.59	12.80	.60
Fat pig, 1,000 lbs. fasted live } weight	17.57	6.92	1.48	6.67	.85
Milk, 1,000 lbs.	6.25	2.03	1.80	1.56	.18
Wool (unwashed), 1000 lbs.	73.00	1.00	40.00	1.00	.70

The character of the food supplied to the farm-stock has, however, the greatest influence in determining the quality of the manure; the more nitrogenous and abundant is the diet, the higher will be the quality of the manure. A third element in determining the character of the manure is the nature and proportion of the litter used.

Supposing the quantity and kind of food and litter consumed on any farm to be known, it is possible to calculate pretty nearly what will be the quantity and composition of the farmyard-manure produced. Lawes and Gilbert have made such a calculation for a farm on the ordinary four-course rotation, assuming that 1 cwt. of oil-cake per acre per annum is consumed by the stock, and that the manure suffers no loss from drainage. The result they arrived at synthetically is given in the next table, with an abstract of the actual analyses of other chemists.

*Percentage Composition of ordinary Farmyard-Manure.*

	Lawes and Gilbert	Boussingault	Voelcker		E. Wolf	Anderson
	Calculated composition of fresh dung	Average composition	Fresh dung	Rotten dung	Average composition	Mean of 8 samples
Water . . . .	70.00	79.30	66.17	75.42	75.00	72.48
Organic matter . .	27.23	14.03	28.24	16.63	18.09	13.94
Ash . . . .	2.77	6.67	5.59	8.05	6.91	13.58
Potash . . . .	.53	—	.67	.49	.68	.32
Phosphoric acid . .	.23	—	.31	.45	.32	.31
Nitrogen . . . .	.64	.41	.64	.61	.53	.38

Lawes and Gilbert's calculated composition for fresh dung is lower in total ash than the actual manure, as this always contains an admixture of sand and earth. Boussingault's results relate to a mixed manure from horses, oxen, and pigs, the decomposition of which was moderately advanced. He found water to vary from 77.8 to 80.4 p.c., and the nitrogen in the dry matter from 1.7 to 2.4 p.c. The fresh dung, analysed by Voelcker, was 14 days old; it was the mixed produce of horses, cows, and pigs. The rotten dung was 6 months old, and of similar origin to the preceding. Anderson's results, relating to the manure of Scotch farms, show great variation and low quality. Water ranged from 58.64 to 83.02; organic matter from 7.24 to 21.68; potash from .10 to .60; phosphoric acid from .09 to .62; nitrogen from .19 to .49 p.c.

The composition of farmyard-manure is greatly dependent on the extent to which it has suffered decomposition, and on the losses of soluble matters which follow exposure to rain. Fermentation speedily commences in fresh dung, and a great loss of organic matter soon takes place; but, except under the influence of rain, the loss of nitrogen is but small. If the dung is exposed to the influence of rain and drainage, the loss of nitrogen and of soluble ash-constituents will, on the other hand, be very great.

Voelcker (*Jour. Roy. Agri. Soc.* 1856, 191) has investigated the losses farmyard-manure suffers during keeping. A considerable bulk of the fresh manure mentioned in the preceding table was kept for one year under cover, a similar bulk was kept for the same time in a heap exposed to weather, and a third portion of the manure was spread as in a yard. Under cover the organic matter fell in 6 months to 52 p.c., and in 12 months to 44 p.c. of the original quantity; but the nitrogen at the end of the year was still 90 p.c. of the original; the manure at the close of the experiment contained only 41.6 p.c. of water. The same manure exposed to weather during 6 winter months of little rain, contained 59 p.c. of its original organic matter; but at the end of the 12 months only 33 p.c. remained. The nitrogen was scarcely altered in the first 6 months, but at the end of 12 months, after a wet summer, it had fallen to 71 p.c. of the original amount. The manure spread in a yard suffered a far greater waste; at the end of one year it contained only 21 p.c. of the organic matter, and 41 p.c. of the nitrogen originally present. It is evident from these results that well-fermented dung is a more concentrated manure than fresh dung, since it has lost considerably in bulk, while but little of the nitrogen and none of the ash-constituents have escaped; on the other hand, if the dung is exposed to weather, and the drainage-water lost, the manure rapidly wastes, and the residue is comparatively worthless. The nitrogen lost by dung not exposed to rain disappears as ammonia and as free nitrogen.

In fresh farmyard-manure the nitrogenous compounds are mostly insoluble in water;

in well-fermented dung the proportion both of soluble nitrogen and of soluble organic matter is considerably greater. Farmyard-manure, even after fermentation, contains only a small part of its nitrogen as ammonia. The phosphates and silica in dung are to a great extent soluble.

The experiments at Rothamsted exhibit the quantitative relations of the manure to the crop produced; it is found that in no case is the whole, or nearly the whole, of the manure recovered in the produce. Thus, on the meadow-land, manure has been applied for 9 years, supplying the nitrogen and ash-constituents contained in 1 ton of hay; the average produce of this manure has been 33 cwts. During the same period the produce without manure has averaged 20 cwts.; the manure has thus actually produced only 13 cwts. per annum, and consequently only about 65 p.c. of the manure has been recovered in the crop. In the case of barley and wheat the relation of the nitrogen applied to the nitrogen found in the increase of the crops has been calculated for a period of 20 years, and in the case of oats for 3 years; the mean results are given below. In each case the crop was abundantly supplied with ash-constituents, and the increase due to the nitrogenous manure has been ascertained by subtracting from the produce yielded by the mixed cinereal and nitrogenous manure that given by the cinereal manure alone:—

*Nitrogen Recovered in the Increase for 100 supplied as Manure.*

Manures applied per acre	Wheat	Barley	Oats
Cinereals and ammonium salts (41 lbs. nitrogen) . .	32.4	48.1	—
" " " (mean 53.3 lbs. nitrogen) . .	—	49.8	—
" " " (82 lbs. nitrogen) . .	32.0	—	51.0
" " " (123 lbs. nitrogen) . .	31.6	—	—
" " " (164 lbs. nitrogen) . .	28.5*	—	—
Cinereals and sodium nitrate (82 lbs. nitrogen) . .	45.3	—	50.4
Cinereals and rape-cake (mean 61.75 lbs. nitrogen) . .	—	36.3	—
Farmyard-manure (about 200 lbs. nitrogen) . .	14.6	10.7	—

It is seen that the nitrogen recovered in the crop is at best only about one-half of that applied in the manure, and that with excessive applications of nitrogen the return is much less. The return is smallest of all in the case of farmyard-manure. This manure does not produce a larger crop than some of the artificial manures mentioned, the amount applied, though large, does not therefore appear to be relatively excessive; the low result is rather due to the fact that the nitrogen of dung exists principally in organic combinations, and becomes available to the plant only by a slow decomposition. In the case of wheat, all the manures, save the sodium nitrate, are applied to the land in the autumn, while in the case of barley and oats the manures are applied in spring-time. The wheat manures thus suffer a loss of winter drainage to which the barley and oat manures are not subject. A great part of the inferior result obtained with wheat is due to this cause, but not the whole of it, as other experiments confirm the statement of the table that barley gives a rather better return for nitrogen applied than wheat. In the rotation experiments the amount of nitrogen recovered in the produce appears to be decidedly larger than with wheat and barley, but details are not yet published.

A crop can never appropriate in one season the whole of the manure applied; for it is impossible that the whole can come in contact with the roots; but in a succession of seasons the whole of the manure should be recovered if none is lost by drainage, by exhalation, or by conversion into inert compounds within the soil. Repeated analyses of drainage-waters have shown that scarcely any phosphoric acid is lost in this direction, all soils containing any ferric oxide or alumina having a powerful retentive power for phosphoric acid. Potash also very seldom appears in drainage-waters, but they are comparatively rich in lime, sulphuric acid, nitric acid, soda, and chlorides. The analyses of the drainage-waters from the wheat-field at Rothamsted (Voelcker, *Jour. Chem. Soc.* 1871, 286, and Frankland, *Jour. Roy. Agr. Soc.* 1878, 387) show that the loss of nitrogen in the form of nitrates may be very considerable. The spring and summer drainage-waters from the plots receiving ammonia contain very little nitric acid, but the winter drainage-waters, following the autumn application of ammonium salts, seldom contain less than 1 part of nitrogen per 100,000, and this in many instances to much larger quantities, the amount being generally proportional to the quantity of ammonia applied. The drainage-water from the plots receiving

\* Mean of 15 years only.

sodium nitrate reaches its maximum contents in nitrates shortly after the spring application of the manure, and in the case of heavy rain the amount thus lost is very considerable. From the plot which has received farmyard-manure for many years very little drainage-water is obtained, owing to the increased porosity of the soil, and it contains less nitric acid than the drainage-waters from any of the ammonia plots, the organic matter of the dung evidently checking oxidation. Lawes and Gilbert calculate that every inch of rain that passes beyond the range of the roots entails a loss of 2.20 lbs. of nitrogen per acre, if the drainage-water contains 1 part of nitrogen per 100,000; and from the evidence yielded by their drain-gauge, they conclude that one-third of the annual rainfall may pass below 40 inches, this drainage being chiefly confined to the winter months. It is quite evident then that a soil will lose a considerable amount of nitrogen by drainage. The great absorptive power of soil for ammonia was formerly thought to ensure the conservation of nitrogen when applied in this form, but the readiness with which ammonia is oxidised into nitric acid in an aerated soil destroys the safeguard just mentioned, and ammonium salts, like nitrates, should not be applied to land till the crop can make speedy use of them.

Besides loss of nitrogen in drainage-waters, some is possibly lost by exhalation. Boussingault found that snow which had lain on a garden bed contained much more ammonia than the snow collected from the neighbouring terrace. A soil rich in organic matter may also evolve nitrogen in a free state. T. Schlösing has shown (*Compt. rend.* lxxvii. 203, 353) that a moist vegetable soil containing nitrates, if confined in a small quantity of air, first absorbs all the oxygen, carbonic acid being produced; that the nitrates are then reduced with formation of ammonia; and that finally a quantity of free nitrogen is evolved in excess of the nitrates originally present, the organic nitrogen of the soil evidently therefore suffering loss. Nitrogen is apparently evolved in the free state during the decomposition of organic bodies only when oxygen has been admitted. Lawes, Gilbert, and Pugh obtained considerable quantities of free nitrogen from the decomposition of moistened beans, &c., when oxygen was admitted, but the gases evolved were only carbonic acid and hydrogen when oxygen was excluded.

The nitrogen of manure may also exist in the soil in a form unsuitable for assimilation by the plant and thus cease to be effective. Nitric acid appears to be pre-eminently the form in which nitrogen is most readily assimilated by plants. Whether ammonia is equally available seems open to doubt, some of the German water-culture experiments exhibiting ammonia as far inferior to nitric acid, while in other cases a normal growth was obtained when ammonia was the only source of nitrogen. The experiments of Cameron, Humpe, Wagner, and others have shown that urea, uric acid, hippuric acid, glycocine, and creatine are perfectly available forms of nitrogen to plants, and in the case at least of urea and creatine, they are taken up without decomposition, being easily detected in the living plant. On the other hand, the nitrogenous humus bodies, which form the bulk of the nitrogenous matter in vegetable soils, are clearly unable to supply nitrogen to plants (at least to cereals), a small quantity of a nitrate far surpassing in its effects a large quantity of nitrogenous peaty matter. By oxidation, and especially by treatment with lime, the nitrogen of the humus becomes, however, slowly available.

In the wheat-field at Rothamsted there is considerable evidence that the residues of ammoniacal manuring speedily assume a form unavailable for succeeding crops of wheat. Plots to which very large quantities of ammonium salts have been applied yield scarcely more produce than unmanured soil as soon as fresh additions of ammonia cease; yet analysis of the soil shows that a considerable accumulation of nitrogen has really taken place. It has been shown by P. Thénard and others, that ammonia is capable of combining with glucose and other vegetable substances at a high temperature, forming dark coloured nitrogenous bodies in which ammonia cannot be detected. Knop found that peat soils by long contact with ammonia absorbed considerable quantities, and that after this absorption it could not be again recovered in the form of nitrogen by treatment with sodium hypochlorite. It seems possible that nitrogenous matters of a similar character may be formed in the soil by the action of the ammonia applied as manure on decaying vegetable substances.

With regard to the ash-constituents of manure there can be little doubt that some of them, especially phosphoric acid, assume more or less insoluble forms after mixing with the soil, and cease to be as available for the plant as a fresh application of manure. The Rothamsted experiments, however, plainly show that residues of mineral manures are capable of producing a marked and long-continued effect on succeeding crops, and that in the case of wheat, residues of phosphates and alkalis are far more effective than residues of ammonia. For details of these results see Lawes and Gilbert's statements (*Jour. Roy. Agri. Soc.* 1873, 321).

From the considerable absorptive power of soil for phosphoric acid and potash, the

residues of these manures remain accumulated near the surface. Hermann v. Liebig (*Jour. Chem. Soc.* 1872, 318, 837) has analysed some of the soil of the Rothemann wheat-field after 22 years' application of manure: he finds the accumulation of phosphoric acid and potash to be chiefly in the first 9 inches of soil, and none has apparently passed below the second 9 inches.

R. W.

**MAXITE.** This name is given by Laspeyres (*J. pr. Chem.* [2], v. 470) to a hydrated sulphato-carbonate of lead found in the Mala-Calzetta mine, near Iglesias in Sardinia, where it occurs in small quantities in galena, together with anglesite ( $\text{PbSO}_4$ ) and cerussite ( $\text{PbCO}_3$ ), forming curvilinear and crystalline masses, with one distinct cleavage-plane to which the acute bisectrix is perpendicular. The cleavage and the optical properties show that the mineral belongs to the rhombic or trimetric system. Besides the principal cleavage, which yields lamellae with adamantine lustre and Newtonian colour-rings, there appear to be also indistinct directions of cleavage. The mineral is negatively uniaxial, with very small axial angle, and strong refractive power, like all native lead-salts; the optic axes are more divergent for the red than for the blue rays. Fracture, conchoidal or splintery. Hardness, 2.5 to 3; that is, between potash-mica and calcsp. Sp. gr. 6.874. Somewhat brittle; colourless, transparent to translucent. Lustre on the fractured surface, fatty-adamantine like that of cerussite. In physical properties, therefore, maxite closely resembles leadhillite ( $3\text{PbCO}_3 \cdot \text{PbSO}_4$ ), but it is distinguished from that mineral by containing water. At  $100^\circ$  it gives off only traces (0.099 p.c.) of hygroscopic water, the constitutional water requiring a heat of  $250^\circ$ – $300^\circ$  to expel it. The carbonic acid requires a still higher temperature, and is not completely expelled below a bright red heat. At the outer edge of an ordinary spirit-flame, maxite fuses quickly and quietly, almost as easily as native sulphide of antimony (which, as v. Kobell has shown, is the most easily fusible of all minerals) to a bead of lead sulphate and oxide, which is red while hot, then becomes yellow, and, on cooling, crystalline and nearly white. Before the blowpipe it gives the ordinary reactions of lead, and when fused with sodium carbonate on charcoal, a strong hepatic reaction.

Quantitative analysis gave results agreeing with the empirical formula,  $5\text{H}_2\text{O}$ ,  $18\text{PbO}$ ,  $9\text{CO}_2$ ,  $5\text{SO}_3$ .

	Calculation		Analysis
$5\text{H}_2\text{O}$ . . . . .	90	1.838	1.866
$9\text{CO}_2$ . . . . .	386	8.081	8.082
$5\text{SO}_3$ . . . . .	400	8.163	8.140
$18\text{PbO}$ . . . . .	4014	81.918	81.912
	4890	100.000	100.000

From this may be deduced the rational formula,  $5\text{PbSO}_4 \cdot 9\text{PbCO}_3 \cdot (4\text{PbO}, 5\text{H}_2\text{O})$ , which is that of a molecular compound of 31 p.c. lead sulphate, 40 p.c. lead carbonate, and 20 p.c. of a lead hydroxide not known in the separate state.

Bertrand (*Bull. Soc. Chim.* [2], xix. 17; *Chem. Soc. J.* [2], xi. 481) regards maxite not as a distinct mineral, but as leadhillite altered by the action of water, and describes a specimen of leadhillite from Iglesias, in which the same alteration has taken place, but to a smaller extent than in the maxite described by Laspeyres (see *LEADHILLITE* (p. 730).

Laspeyres, on the other hand (*Jahrb. f. Mineralogie*, 1873, 292; *Chem. Soc. J.* [2], xi. 1112), points out that the difference of composition between maxite and leadhillite is much too great to allow of their being regarded as identical, as, indeed, may be seen by the following comparison:—

	PbO	CO <sup>2</sup>	SO <sup>3</sup>	H <sup>2</sup> O
Maxite . . . . .	81.912	8.082	8.140	1.866
Leadhillite (Scotch) . . . . .	80.800	11.950	7.250	—
Difference . . . . .	+1.112	—3.868	+0.890	—1.866

These differences become still more apparent on writing the formulae  $(18\text{PbO}, 9\text{CO}_2, 5\text{SO}_3 + 5\text{H}_2\text{O})$  and that of leadhillite ( $4\text{PbO}, 3\text{CO}_2, 1\text{SO}_3$ ) in terms of molecules of lead oxide; they then become—

	PbO	CO <sup>2</sup>	SO <sup>3</sup>	H <sup>2</sup> O
Maxite . . . . .	36	18	16	1
Leadhillite . . . . .	36	27	5	—
Difference . . . . .	0	—9	+11	—1

Laspeyres is further of opinion that the so-called leadhillite from Iglesias is maxite.

by Bertrand, is not leadhillite more or less altered by hydration, but a mixture of true leadhillite with *marcasite*.

**MELAMPYRUM.** The seed of the Purple Cow-wheat (*Melampyrum arvense*) contains a glucoside identical with, or very much like, rhinanthin (1st Suppl. 994). It is obtained by exhausting the seeds with alcohol, freeing the extract from fat, and leaving the alcoholic solution to evaporate over sulphuric acid; by a second crystallisation it is obtained white. When boiled with an acid, it splits up into glucose and an insoluble violet-brown substance (H. Ludwig and H. Müller, *Arch. Pharm.* [2], cxlix. 6).

**MELAPHYRE.** The melaphyres of the Little Carpathians have been examined by H. Höfer (*Jahrbuch f. Mineralogie*, 1871, 113). They are eruptive rocks of the middle trias period, and may be classified as compact, crystalline, porphyritic and amygdaloidal.

1. *Compact*.—This is the predominating variety of the group, and is distinguished by its varied colour, the darker hues, however, prevailing. The typical colour is black, with a dash of violet; red and reddish-brown are rare, and black passing into green is frequent. By weathering, the latter hue changes to a light yellowish-brown, through the oxidation of ferrous oxide. The green varieties effervesce more with acid than the black, and this is especially the case with freshly-exposed dark green specimens. The green melaphyre takes a black colour and almost metallic lustre by weathering. By aid of a lens, numerous dark green granules, resembling selenonite, are observed in it. Compact melaphyre melts before the blowpipe to a black and very vesicular slag; has a stony conchoidal fracture, and a hardness between 6 and 7. Though hand specimens but slightly affect the magnetic needle, this instrument is entirely untrustworthy in the vicinity of the rocks themselves. The specimens examined were: I. Violet-black melaphyre, from the southern end of the Blumenthal, north of Gronitz; sp. gr. 2.852. II. Blackish-grey melaphyre, with a dash of olive-green, resembling basalt, from the bed of the Schwarzen Waag, near Hoskova; sp. gr. 2.734:

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	CaO	MgO	K <sup>2</sup> O	Na <sup>2</sup> O	CO <sup>2</sup>	H <sup>2</sup> O	Total
Ia.*	52.75	10.80	20.24	3.84	2.36	0.41	1.54	3.62	1.99	3.10	100.65
Ib.	56.20	11.30	21.18	4.02	2.47	0.43	1.61	3.79	—	—	100.00
IIa.	50.41	21.40	11.07	4.95	3.31	0.94	2.26	3.91	—	3.33	101.58
IIb.	51.31	21.78	11.26	5.04	3.37	0.96	2.30	3.98	—	—	100.00

The oxygen ratios of silica, sesquioxides, and protoxides are in Ib: 29.438, 11.620, 3.009; and in IIb: 27.364, 13.556, and 3.865.

2. *Crystalline*.—This variety is in a state of transition from the compact to the porphyritic variety; bright coloured scales separate themselves from the uniform mass, and when of some size are recognised as felspar; the conchoidal fracture is lost, and becomes irregular. If the crystals of felspar increase in size, the rock is then porphyritic, and the three forms of melaphyre are occasionally met with, side by side, *in situ*. The lithological characters of the crystalline varieties are, as regards colour, as varied as those of the compact melaphyres, to each of which, in fact, a congeneric crystalline kind is to be met with.

The specimen examined was from the Ipoliczathal, near Hoskova. It was green; had a sp. gr. = 2.860, and enclosed very small white brilliant crystals, apparently of felspar, green, often foliated, masses, intimately mixed with the felspar, and occasional black, angular granules. Its composition is:—

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	CaO	MgO	K <sup>2</sup> O	Na <sup>2</sup> O	H <sup>2</sup> O	Total
a.	48.60	12.81	10.77	9.43	7.99	0.99	1.66	5.56	3.36	99.26
b.	50.77	13.37	11.23	9.84	8.33	1.03	1.73	5.71	—	100.00

The oxygen ratios of silica, sesquioxides, and protoxides are: 27.076, 8.610, and 6.203.

3. *Porphyritic*.—The dark varieties and those with a violet hue are, with scarcely an exception, the only ones which become entirely porphyritic. This division, there-

\* In this and the following tables the percentages given under a are the direct results of analysis, those under b are raised to 100° after deduction of carbonic anhydride and water.

fore, is characterised by a blackish-violet base, enclosing greenish felspar in crystals, on an average 6 lines in length and 1 line in breadth.

The composition of a specimen of the above kind, found south of Lucavina, at the north foot of the Palkniczaberg, is given below (I), as well as that of the light green felspar (andesin) which it encloses (II), and of the dark violet base itself (III).

	SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	FeO	CaO	MgO	K <sup>a</sup> O	Na <sup>a</sup> O	H <sup>a</sup> O	Total	Sp. gr.
Ia. . .	52.46	19.65	10.86	1.92	5.30	0.65	1.57	2.89	4.81	100.11	2.689
Ib. . .	55.05	20.62	11.40	2.01	5.56	0.68	1.65	3.03	—	100.00	—
IIa. . .	53.26	24.28	—	2.96	6.83	0.56	2.47	4.68	3.08	99.02	2.633
IIb. . .	56.04	25.55	—	3.12	7.19	0.59	2.59	4.91	—	100.00	—
IIIa. . .	50.65	16.32	15.03	2.33	4.45	0.63	1.79	3.44	5.14	99.78	2.761
IIIb. . .	53.62	17.25	15.88	2.46	4.70	0.67	1.89	3.63	—	100.00	—

The oxygen ratios of silica, sesquioxides, and protoxides, are: Ib. 29.358, 13.139, and 3.552; IIb. 29.886, 11.943, and 4.681; and IIIb. 28.542, 12.822, and 3.397.

A further example of this variety, from an entirely isolated out-crop in the Bistrital, near Bries, enclosed green crystals of felspar, and round masses,  $1\frac{1}{2}$  lines across, of a green, almost compact mineral, which was found to be dellesite, enclosing small particles of calcite. This rock has a rather even splintery fracture, and is probably in the first stage of decomposition. Its specific gravity is 2.816, and composition:—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	FeO	CaO	MgO	K <sup>a</sup> O	Na <sup>a</sup> O	CO <sup>a</sup>	H <sup>a</sup> O	Total
52.21	12.84	16.35	5.67	3.67	1.13	0.98	1.90	2.01	4.50	101.26
56.10	13.55	17.26	6.00	3.87	1.19	1.03	2.00	—	—	100.00

The oxygen ratios of silica, sesquioxides, and protoxides, are: 29.385, 11.506, and 3.589.

4. *Amygdaloidal*.—The numerous varieties of this group agree in having a dark base. In one from the Nischne Chmelenithal, at Svarin, it was of a dull dirty violet, and enclosed felspar crystals  $1\frac{1}{2}$  lines in length, which had lost their distinct cleavage, were without lustre, and effervesced with acid. In some of the more altered crystals small spherules of a dark green mineral are seen; in other instances the entire structure of a crystal has been replaced by this substance. The amygdaloids, then, are clearly due to a metamorphosis of the andesin.

The specific gravity of this altered melaphyre is 2.856, and its composition is given below, under I.

A typical specimen from Schwarzwaag had a dull reddish-brown base, enclosing dellesite, amygdaloids of calcite, and here and there small particles of mesitin. The felspar was completely decomposed. Its specific gravity is 2.727, and composition as under (II):—

	SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	FeO	CaO	MgO	K <sup>a</sup> O	Na <sup>a</sup> O	CO <sup>a</sup>	H <sup>a</sup> O	Total
Ia. . .	51.80	7.78	20.90	5.34	3.10	0.47	2.25	2.71	1.29	3.77	99.60
Ib. . .	54.85	8.24	22.23	5.65	3.28	0.50	2.38	2.87	—	—	100.00
IIa. . .	42.75	14.04	14.10	2.50	9.10	0.57	2.22	4.29	7.69	3.49	100.75
IIb. . .	47.73	15.67	15.74	2.79	10.16	0.64	2.48	4.79	—	—	100.00

The oxygen ratios of silica, sesquioxides, and protoxides, are: Ib. 29.252, 10.414, and 3.523; and IIb. 25.454, 12.042, and 5.411.

The minerals met with in the larger cavities of the altered melaphyre of this region are: dellesite and green earth, calcite, mesitin, quartz, chalcedony, agate, and jasper, pistacite, heulandite, copper pyrites, and malachite.

**MELLITIC ACID, C<sup>12</sup>H<sup>4</sup>O<sup>12</sup>.** The principal results of Beeyer's elaborate investigation of this acid and its derivatives have been given in the *Ann. Chem. Phys.* (pp. 808-814). The following facts have since been published (*Ann. Chem. Phys.* xlvii. 325-360).

The acid C<sup>12</sup>H<sup>4</sup>O<sup>12</sup> = C<sup>6</sup>H<sup>2</sup>(COOH)<sup>4</sup>, formerly called hydropyromellitic acid, is



mixture of two isomerides. One of these, for which the original name is retained, is amorphous, while the other, called *isohydropyromellitic acid*, crystallises in agglomerations of needles having the composition  $C^{10}H^{10}O^3 \cdot 2H^2O$ , and giving off their water of crystallisation at  $120^\circ$ . Its aqueous solution is not precipitated by baryta-water in the cold, but on heating the liquid, a dense crystalline precipitate soluble in acetic acid is formed. Lead acetate produces a flocculent precipitate insoluble in acetic acid.

Both varieties of hydropyromellitic acid, when heated above  $200^\circ$ , yield a distillate of tetrahydrophtalic acid,  $C^8H^{10}O^4$  (see PHTHALIC ACID).

When mellitic acid is heated with *glycerin* till the solid mass becomes brownish-black and porous, no pyromellitic acid is formed, but a large quantity of trimesic acid,  $C^6H^4O^6$ .

*Trimellitic acid*,  $C^6H^2(CO^2H)^3$ , when heated, yields the anhydride  $C^6H^2 \begin{Bmatrix} CO > O, \\ CO > O, \\ COOH \end{Bmatrix}$

a crystalline mass which melts at  $157^\circ$ – $158^\circ$ , and dissolves readily in hot water.

*Prehnitic anhydride*, formed in like manner from prehnitic acid,  $C^6H^2(CO^2H)^4$ , has the composition  $C^6H^2 \begin{Bmatrix} CO > O. \\ CO > O. \\ (COOH)^2 \end{Bmatrix}$

The *methylic ethers* of the several polycarbonic acids of benzene crystallise exceedingly well, and are well adapted for the detection and comparison of these acids. The following have been prepared by the action of methyl iodide on their silver salts.

*Methyl isohydropyromellitate* crystallises from a hot alcoholic solution in short thick needles, melting at  $156^\circ$ , and distilling without decomposition. *Methyl pyromellitate* is but sparingly soluble in boiling alcohol, and forms large plates melting at  $138^\circ$ .

*Methyl trimellitate* crystallises from dilute alcohol in long slender needles melting at  $63^\circ$ – $65^\circ$ .

**MELOLONTHIN**,  $C^8H^{12}N^2SO^3$  (P. Schreiner, *Deut. Chem. Ges. Ber.* iv. 763). A crystallisable substance obtained together with leucine, sarcosine, doubtful traces of xanthine, abundance of water, and calcium oxalate, from cockchafer (Melolontha vulgaris). The aqueous extract of the mashed insects is freed from albuminoids by boiling; the concentrated filtrate is precipitated by basic lead acetate; and the filtered liquid, freed from excess of lead by hydrogen sulphide, is concentrated, whereupon it deposits urates. The mother-liquor evaporated to a syrup and left at rest for some time deposits crystals which exhibit under the microscope well-defined needles, together with the spherical forms of leucine, and the mother-liquor after a few days yields a second crop of the needles. The united products are treated, first with a large quantity of alcohol of 80 p.c., then for a considerable time with alcohol of 70 p.c., whereby the leucine is dissolved and a white flocculent substance consisting of microscopic needles is left behind. These needles also separate from the 70 p.c. alcohol during the filtration.

The substance thus obtained is melolonthin. 30 lbs. of cockchafer yield only 1.56 gram of it. When purified by recrystallisation from water, with addition of a few drops of ammonia, it is perfectly colourless, and has a beautiful silky lustre. It is tasteless and scentless; hard; grates between the teeth; does not lose weight at  $100^\circ$ ; dissolves sparingly in cold, more easily in warm water, very slightly in aqueous alcohol, not at all in absolute alcohol or in ether, but easily in potash, soda, sodium carbonate, ammonium carbonate, tartaric, hydrochloric, nitric, and sulphuric acids, and in water containing a few drops of ammonia; and crystallises from this last-mentioned solution, as the ammonia evaporates, in rather large tabular rhombic prisms. The aqueous solution does not act on polarised light.

**MENEGBNITE**. This mineral, hitherto found only at Bottino in Tuscany, has been discovered in the emery bed at Ochsenkopf near Schwarzenberg in Saxony. It occurs in compact masses disseminated through the emery; has a metallic lustre, a black lead-grey colour, a black shining streak, compact to even fracture; hardness = 3; sp. gr. = 6.387. Two analyses gave—

Lead	Copper	Antimony	Sulphur	Iron	
61.33	1.38	19.60	17.04	—	= 99.35
60.09	1.56	19.11	18.22	0.25	= 99.23

indicating the formula  $4PbS.Sb^2S^3$ , which is that previously assigned to meneghinite (iii. 879; Frenzel, *Jahrbuch f. Mineralogie*, 1871, 200).

**MERCURY**. *Tension and Diffusion of Mercury Vapour*.—Faraday showed that mercury gives off vapour at ordinary temperatures between  $15.5^\circ$  and  $27^\circ$ ; but his experiments did not indicate the formation of mercurial vapour at temperatures below the freezing point of water (iii. 864). Merget, however (Compt. rend. lxxiii. 1356), by 2nd Sup.

exposing paper streaked with ammoniacal silver nitrate, or in bright sunshine the chlorides of platinum and palladium, to the action of the mercury vapour, has shown that the vaporisation of the metal goes on continuously between  $+25^{\circ}$  and  $-25^{\circ}$ , and takes place even as low as  $-44^{\circ}$ , not being interrupted even by the freezing of the metal, and that the vapours possess a considerable diffusive power.

Regnault (*Compt. rend.* lxxiii. 1402) also finds that mercury at  $-13^{\circ}$  gives off sufficient vapour to produce a daguerreotype picture by 24 hours' exposure. His determinations of the vapour-tension of mercury at different temperatures (iii. 94) also show that it emits vapour of measurable tension at  $0^{\circ}$ .

**Estimation.**—Two processes for the estimation of mercury are given by J. B. Hannay (*Chem. Soc. J.* [2], xi. 565). The first, which is a volumetric method, depends upon the fact that potassium cyanide dissolves the precipitate produced by ammonia in a solution of mercury chloride. A few drops of ammonia are first added to the solution containing the mercury in the state of chloride, and then a standard solution of potassium cyanide until the turbidity produced by the ammonia disappears. If arsenic, copper, &c., be present, the solution should be precipitated by sulphuretted hydrogen, the arsenic, &c., separated by sulphide of ammonium, and the mercury sulphide dissolved in aqua regia.—The other method consists in decomposing the mercury, in solution as sulphate, by the electric current in a platinum basin, the mercury being deposited on the basin in the state of metal and weighed as such.

Eshka (*Dingl. polyt. J.* civ. 47) estimates mercury in its ores by exposing the ore to a high temperature in contact with metallic iron, and absorbing the volatilised mercury with metallic gold.

A weighed portion of the pulverised sample is placed in a porcelain crucible, with smooth and even edge, and mixed with about half its weight of pure iron filings, and the whole is uniformly covered with a layer of filings from 0.5 to 1 centim. thick. The crucible is covered with a concave, well-fitting gold lid, the cavity of which is filled with distilled water. The crucible is heated for ten minutes by means of a flame, whose point plays on the under surface. The gold lid is now removed from the crucible, the water poured off, and the mercurial mirror on the convex side is washed with alcohol, the lid dried in the water bath, and weighed after cooling. The increase of weight in the gold lid expresses the weight of mercury contained in the sample of ore.

The quantity of ore to be operated on varies from 10 grams for poor ores containing 1 p.c. of mercury to 1 gram for rich ores about 30 p.c.

**Amalgams.**—Crystalline amalgams of potassium and sodium are described by Kraut & Popp (*Ann. Ch. Pharm.* clix. 188). When sodium amalgam (prepared by triturating 3 parts of sodium with 97 parts of mercury) is added to an aqueous solution of carbonate or hydrate of sodium, or left for several days under a moderate quantity of water, long needles of an amalgam are formed having the composition  $\text{Na}^{\text{I}}\text{Hg}^{\text{I}}$ . If the sodium amalgam be immersed in a solution of carbonate or hydrate of potassium, hard crystals appear after a few days in the separated mercury, consisting of an amalgam of potassium. These crystals are cubes with rhombic dodecahedral and octohedral faces, the sides of which sometimes attain the length of 5 mm. When left under the liquid they disappear again for some time, but in closed vessels they remain unaltered. They contain mercury, potassium, and sodium, the quantity of the sodium being less the longer the time for which the formation of the crystals has gone on. Supposing the sodium to be in the form of the above described amalgam  $\text{Na}^{\text{I}}\text{Hg}^{\text{I}}$ , merely mixed with the potassium amalgam, the composition of the latter will be expressed by the formula  $\text{K}^{\text{I}}\text{Hg}^{\text{I}}$ . These formulae of the potassium and sodium amalgams exhibit some analogy to those of the peroxides of the same metals, viz.  $\text{K}^{\text{O}}\text{O}^{\text{I}}$  and  $\text{Na}^{\text{O}}\text{O}^{\text{I}}$ . Crystallised potassium amalgam was prepared some time ago by Berzelius and Pontin (iii. 889), also by Crookewite (*Jahresb. f. Chem.* 1847-48, 893). Löwig (*ibid.* 1860, 397) obtained sodium amalgam in prisms an inch long by adding sodium to mercury in such quantity that the mixture solidified completely on cooling, then pressing out the excess of mercury, fusing the amalgam, and leaving it to solidify slowly.

**Reactions of Mercury Compounds.**—A solution of mercuric chloride is completely decomposed in a few hours at ordinary temperatures by metallic silver (especially in the finely divided state) according to the equation—



From a solution of mercuric iodide in potassium iodide, silver likewise precipitates the mercury completely at ordinary temperatures (Campani, *Nuovo Cimento* [2], iii. 73).

Mercuric oxide dissolves completely in solution of potassium iodide, in consequence

of the formation of potassium hydrate and the double iodide  $2\text{KI.HgI}^2$  (John, *Arch. Pharm.* [3], i. 97).

**Mercuric sulphide.**—This compound occurs in Lake County, California, forming an amorphous crust in clefts and hollows of a siliceous gangue, associated with cinnabar and with iron- and copper-pyrites. Fracture, conchoidal to brittle; hardness = 3; sp. gr. = 7.701–7.748; colour, greyish-black; streak on porcelain, pure black. Before the blowpipe it behaves like cinnabar. The mean of several analyses gave—

S	Hg	Fe	Quartz
13.82	85.79	0.39	0.25 + 100.25

the formula  $\text{HgS}$  requiring 13.88 sulphur and 86.12 mercury (G. Moore, *Jahrbuch f. Mineralogie*, 1871, 201).

**MERCURY-RADIOLES, ORGANIC.** See 1st Suppl. (pp. 818–821). On the Naphthyl-mercuric Compounds, see further NAPHTHYL, in this volume.

**MESACONIC ACID,  $\text{C}^6\text{H}^4\text{O}^4$ .** On the formation of this acid from the isomeric itaconic acid, see p. 709.

Potassium mesaconate subjected to electrolysis yields at the positive pole carbon dioxide and allylene,  $\text{C}^3\text{H}^2$ , which is precipitated by silver nitrate. The other products of the decomposition are probably acrylic and itaconic acids. The allylene thus produced is not identical either with ordinary allylene, or with those produced respectively by the electrolysis of citraconic and itaconic acid (p. 708).

Mesaconic acid is slightly coloured by ferric chloride, and the solution when boiled deposits a gelatinous precipitate which redissolves on cooling. The addition of a further quantity of ferric chloride prevents its redissolution. Neutral mesaconates of alkali-metal give with ferric chloride a brown precipitate which is insoluble in excess of the reagents, and does not dissolve when the liquid is heated (Aarland, *J. pr. Chem.* [2], vi. 256).

**MESITYLENE,  $\text{C}^6\text{H}^{12} = \text{C}^6\text{H}^4(\text{CH}^3)^2$ .** This hydrocarbon, treated with phosphonium iodide, is hydrogenised more easily than benzene, toluene, or xylene (p. 656), and is converted into hexhydromesitylene,  $\text{C}^6\text{H}^{12}$ . The latter, when freed by nitric acid from unaltered mesitylene, boils at  $135^\circ$ – $138^\circ$ ; it smells like petroleum, is attacked by bromine, and converted by prolonged treatment with fuming nitric acid into triinitromesitylene (A. Bayer, *Ann. Ch. Pharm.* clvi. 266).

**MESITYLENE-SULPHONIC ACID,  $\text{C}^6\text{H}^{12}\text{SO}^3 = \text{C}^6(\text{CH}^3)^2\text{H}^2\text{SO}^3\text{H}$**  (Jacobsen, *Ann. Ch. Pharm.* cxlv. 85). The mesitylene required for the preparation of this acid was obtained by a modification of Fittig's process (1st Suppl. 298). Instead of first mixing the acetone with sand and then adding sulphuric acid, the acetone (2 vol.) was at once mixed with strong sulphuric acid in a retort fitted with a long condensing tube directed upwards, so that the acetone volatilised by the heat resulting from the action might flow back again; the liquid after cooling was mixed with a quantity of sand sufficient to form a thick paste, and then distilled. A kilogram of acetone thus treated yields 110 grams of crude mesitylene boiling between  $163^\circ$  and  $170^\circ$ .

To prepare the sulphonic acid, this crude mesitylene was treated with a mixture of ordinary and fuming sulphuric acid in equal volumes, whereupon it dissolved with only slight browning and almost without rise of temperature, the solution beginning to crystallise after a few minutes, and soon afterwards solidifying completely. A small quantity of another hydrocarbon, probably a tetramethyl-benzene, remained undissolved; it dissolved, however, in warm fuming sulphuric acid, yielding a sulphonic acid whose salts were essentially different from these mesitylene-sulphonates. For the preparation of mesitylene-sulphonic acid it would therefore be better to digest the impure mesitylene only with ordinary sulphuric acid.

The aqueous solution of the mesitylene-sulphonic acid, prepared as above described, yielded directly a very pure barium salt, which was recrystallised and used for the preparation of the other mesitylene-sulphonates.

Mesitylene-sulphonic acid is obtained, by slow evaporation of its syrupy solution over sulphuric acid, as a coarsely laminar crystallised mass having the composition  $\text{C}^6\text{H}^{12}\text{SO}^3 \cdot 2\text{H}^2\text{O}$ . The individual crystals are six-sided tables (Jacobsen). According to H. Rose (*Zeitschr. f. Chem.* [2] vi. 341), they belong to the rhombic system, and the salts, especially the magnesium salt  $\text{Mg}(\text{C}^6\text{H}^{12}\text{SO}^3)^2 + 6\text{H}^2\text{O}$ , which crystallises in large hard transparent tables, very much resemble the acid in their forms. According to Jacobsen, the acid is not deliquescent, melts near  $100^\circ$ , and is resolved at a higher temperature into mesitylene and sulphuric acid. According to Rose, it melts near  $77^\circ$ , attracts moisture only in very damp air, solidifies again in the crystalline form in dry air, and gives off its water of crystallisation when kept for a long time over sulphuric acid.

*Potassium Mesitylene-sulphonate*,  $\text{KC}^6\text{H}^3\text{SO}^3 + \text{H}^2\text{O}$ , usually crystallises in roundish groups of laminae having a silky lustre; it dissolves in 7 parts of water at  $12^\circ$ , somewhat less abundantly in cold alcohol; in both cases the solubility diminishes very rapidly with the temperature. From the alcoholic solution the salt is gradually precipitated by ether in spherical aggregates. The *ammonium salt*,  $(\text{NH}^4)^+\text{C}^6\text{H}^3\text{SO}^3 + \text{H}^2\text{O}$ , is very soluble in water and in alcohol, and crystallises by slow cooling in rhombic plates. It gives off its water of crystallisation at  $110^\circ$ , melts with decomposition at  $250^\circ$ , and yields a sublimate of a substance which is insoluble in water, easily soluble in alcohol, and still more in ether, and probably consists of mesitylene-sulphamide. The *calcium salt*,  $\text{Ca}(\text{C}^6\text{H}^3\text{SO}^3)^2 + 5\text{H}^2\text{O}$ , forms distinct, hard, limpid crystalline crusts which effloresce in dry air. The *strontium salt*, which may be obtained in stellate groups of large laminae, likewise gives off its water with facility. The *barium salt*,  $\text{Ba}(\text{C}^6\text{H}^3\text{SO}^3)^2 + 9\text{H}^2\text{O}$ , crystallises from a moderately concentrated hot solution in long flat prisms with dihedral summits, or by slower crystallisation in more tabular, shorter, but broader crystals; from alcohol in bright iridescent laminae. It dissolves in 15 parts of water at  $28^\circ$ , the solubility increasing quickly with the temperature. It effloresces very easily in dry air, gives off 8 mol. water at a comparatively low temperature, but retains the last molecule till it is heated above  $100^\circ$ . The *cobalt salt*,  $\text{Co}(\text{C}^6\text{H}^3\text{SO}^3)^2 + 6\text{H}^2\text{O}$ , crystallises in beautiful groups of shining flesh-coloured laminae, easily soluble in water and in alcohol. When dried at  $100^\circ$  it is rose-red and still appears to retain  $4\text{H}^2\text{O}$ ; the dehydrated salt is of a fine ultramarine colour. The *copper salt*,  $\text{Cu}(\text{C}^6\text{H}^3\text{SO}^3)^2 + 4\text{H}^2\text{O}$ , crystallises in spherical groups of whitish-green laminae having a silky lustre; after drying at  $100^\circ$  it is grass-green and anhydrous. It dissolves in 17 parts water at  $10^\circ$ , much more freely in hot water. The concentrated solution of the *lead salt*,  $\text{Pb}(\text{C}^6\text{H}^3\text{SO}^3)^2 + 9\text{H}^2\text{O}$ , solidifies on cooling to a coarsely laminar crystalline mass having a strong mother-of-pearl lustre. It dissolves in 6.4 parts of water at  $20^\circ$ , easily also in alcohol, effloresces very quickly, begins to decompose at about  $200^\circ$ . The lead salt crystallising in needles described by Hofmann (*Chem. Soc. J.* ii. 113) was not obtained by Jacobsen.

The acid obtained from the above-mentioned less soluble hydrocarbon mixed with the mesitylene, was produced in comparatively large quantity from the portion of the crude mesitylene which distilled above  $180^\circ$ . The distillate obtained between  $180^\circ$  and  $230^\circ$  was repeatedly rectified over sodium, and the portion boiling between  $195^\circ$  and  $210^\circ$ , probably tetramethylbenzene,  $\text{C}^6\text{H}^{14}$ , was collected apart and dissolved in fuming sulphuric acid. The *barium salt* prepared by saturating the acid liquid with barium carbonate, probably  $\text{Ba}(\text{C}^6\text{H}^3\text{SO}^3)^2 + \text{H}^2\text{O}$ , separated, on evaporating the filtrate, in sparingly soluble, hard, indistinctly crystalline crusts, floating on the surface. The same salt was gradually precipitated in the crystalline state from the solution of the potassium salt by barium chloride. It is very much like barium isocumene-sulphonate, but much less soluble, and its solubility is but little increased by heat. The *potassium salt* is easily soluble in water, and crystallises from the hot alcoholic solution in small felted needles (Jacobsen).

**Bromomesitylene-sulphonic acid**,  $\text{C}^6\text{H}^3\text{BrSO}^3\text{H} = \text{C}^6(\text{CH}^3)\text{HBrSO}^3\text{H}$  (H. Rose, *loc. cit.*) Bromine acts strongly on mesitylene-sulphonic acid, producing, however, for the most part, scarcely anything but brominated substitution-products of mesitylene. It is only by great dilution, efficient cooling, and the use of bromine-water, that any considerable quantity of bromomesitylene-sulphonic acid can be obtained. The liquid filtered from separated bromomesitylene and neutralised with lead carbonate first deposits crystals of lead bromide; and on precipitating the remainder of the lead with hydrogen sulphide, repeatedly evaporating, saturating with barium carbonate, evaporating, and treating the residue with hot alcohol, barium bromomesitylene-sulphonate is dissolved, while any barium bromide that may still be present is left behind. From this barium salt the acid may be prepared in the usual way. The brominated acid may also be obtained, and in somewhat larger quantity, by the action of sulphuric acid on bromomesitylene. The salts of the brominated acids prepared by these two processes exhibit identical properties.

Bromomesitylene-sulphonic acid is very soluble in water, alcohol, and ether, and crystallises from ether in shining needles, which are so deliquescent that their melting-point cannot be determined. Its salts are less soluble than those of mesitylene-sulphonic acid, do not effloresce in dry air, and do not readily give up their water of crystallisation below  $130^\circ$ . Their forms, which are well defined, belong to the rhombic system. The *barium salt*,  $\text{Ba}(\text{C}^6\text{H}^3\text{BrSO}^3)^2 + \text{H}^2\text{O}$ , crystallises in broad needles or laminae, very slightly soluble in alcohol, insoluble in ether. The water of crystallisation is given off only at a temperature near that at which the salt begins to decompose. The *lead salt*,  $\text{Pb}(\text{C}^6\text{H}^3\text{BrSO}^3)^2 + 1\frac{1}{2}\text{H}^2\text{O}$ , forms beautiful radiate groups of crystals, moderately soluble in hot alcohol, insoluble in ether. The *potassium salt*,

$\text{K}^+\text{C}^+\text{H}^{10}\text{BrSO}_3^- + \text{H}_2\text{O}$ , crystallises in isolated rhombic tablets easily soluble in water and in hot alcohol. The *copper salt*,  $\text{Cu}(\text{C}^+\text{H}^{10}\text{BrSO}_3^-)_2 + 4\text{H}_2\text{O}$ , crystallises in beautiful tufts of long, nearly white crystals, having a silky lustre, and assuming a grass-green colour when heated above  $100^\circ$ . The *sodium salt*,  $\text{NaC}^+\text{H}^{10}\text{BrSO}_3^-$ , is obtained, by spontaneous evaporation of its aqueous solution, in hard, finely-developed transparent crystals.

**Nitromesitylene-sulphonic acid**,  $\text{C}^+\text{H}^{10}\text{NO}_2^+\text{SO}_3^-\text{H} = \text{C}^+(\text{CH}_3)^3\text{H}(\text{NO}_2^+)\text{SO}_3^-\text{H}$  (H. Rose, *Zeitschr. f. Chem.* [2], vi. 74). This acid is prepared by gradually adding mesitylene-sulphonic acid to carefully cooled fuming nitric acid, whereupon it dissolves, forming a deep brown solution, which after a few hours becomes almost colourless. This solution is poured into a large quantity of water, filtered from the white flocks of dinitromesitylene which separate together with a small quantity of an oil, probably impure nitromesitylene, and repeatedly evaporated at  $100^\circ$  with addition of water, in order to remove the excess of nitric acid. The crystalline mass, after being pressed and recrystallised, readily yields the pure acid in brittle, transparent, prismatic crystals, having the composition  $\text{C}^+(\text{CH}_3)^3\text{HNO}_2^+\text{SO}_3^-\text{H} + 1\frac{1}{2}\text{H}_2\text{O}$ , easily soluble in water, alcohol, and ether, and melting at  $131^\circ$ . Exposure to sunlight turns the acid yellow, and when dried over sulphuric acid it becomes opaque, and loses its water of crystallisation. Most of its salts are easily soluble in water, crystallise well, and burn with deflagration.

The *barium salt*,  $\text{Ba}[\text{C}^+(\text{CH}_3)^3\text{HNO}_2^+\text{SO}_3^-]_2$ , crystallises from its hot aqueous solution in pale yellow tufts of crystals. It is almost insoluble in ether, soluble with difficulty in cold water and in alcohol. The *potassium salt*,  $\text{KC}^+(\text{CH}_3)^3\text{HNO}_2^+\text{SO}_3^- + \text{H}_2\text{O}$ , forms large white needles or broad plates, and is readily soluble in alcohol and water. The *copper salt*,  $\text{Cu}[\text{C}^+(\text{CH}_3)^3\text{HNO}_2^+\text{SO}_3^-]_2 + 3\text{H}_2\text{O}$ , crystallises in pale green lustrous scales, which are moderately soluble in cold water. The *lead salt*,  $\text{Pb}[\text{C}^+(\text{CH}_3)^3\text{HNO}_2^+\text{SO}_3^-]_2 + \text{H}_2\text{O}$ , is easily soluble in water, and crystallises from hot solutions in white glistening tufts of needles. The *ammonium salt* is readily soluble in alcohol and water, and separates in nodular concretions.

Nitromesitylene-sulphonic acid has not hitherto been produced by the action of sulphuric acid on nitromesitylene.

**Amidomesitylene-sulphonic acid**,  $\text{C}^+(\text{CH}_3)^3\text{HNNH}^+\text{SO}_3^-\text{H} + \text{H}_2\text{O}$ , is prepared from the nitro-acid by dissolving it in ammonia, saturating the solution with sulphuretted hydrogen, and evaporating it almost to dryness; water is then added, and the boiling solution decomposed by hydrochloric acid. The filtered solution, on cooling, deposits the amidomesitylene-sulphonic acid in pale red needles, which may be rendered white by treatment with animal charcoal and recrystallisation. The acid dissolves easily in hot alcohol, with difficulty in cold water, but much more readily in hot water. By slowly cooling its aqueous solution, it is obtained in fine truncated prisms, and from a hot concentrated solution, in needles, which acquire a red tinge on exposure to light. It loses its water of crystallisation when dried over sulphuric acid. It does not combine with hydrochloric acid, and crystallises unchanged from moderately strong sulphuric acid. Its solutions redden litmus-paper, and it expels carbonic acid from the carbonates.

Its salts crystallise well, and are generally easily soluble; their solutions become yellow on evaporation, from incipient decomposition. The *barium salt*,  $\text{Ba}[\text{C}^+(\text{CH}_3)^3\text{HNNH}^+\text{SO}_3^-]_2$ , crystallises from its hot aqueous solution in yellow nodules, which are moderately soluble in cold water. The *magnesium salt*,  $\text{Mg}[\text{C}^+(\text{CH}_3)^3\text{HNNH}^+\text{SO}_3^-]_2 + 3\text{H}_2\text{O}$ , forms hard transparent yellow crystals. The *zinc salt*,  $\text{Zn}[\text{C}^+(\text{CH}_3)^3\text{HNNH}^+\text{SO}_3^-]_2 + 5\text{H}_2\text{O}$ , is readily obtained in fine crystals, easily soluble in cold water. The *lead salt*,  $\text{Pb}[\text{C}^+(\text{CH}_3)^3\text{HNNH}^+\text{SO}_3^-]_2 + \text{H}_2\text{O}$ , is also readily soluble in cold water, and crystallises well. The *calcium, sodium, and ammonium salts* are readily soluble in cold water; the *silver salt* much less soluble (H. Rose).

**MESOCAMPHORIC ACID.** See CAMPHORIC ACID (p. 235).

**MESOLE.** Pisani (*Compt. rend.* lxxiii. 1448) has analysed a mesole from the basaltic amygdaloid of Gignat, near Saint-Germain-Lembron in Auvergne, with the following results:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$
42.3	28.1	10.0	6.7	trace	14.1 = 101.2

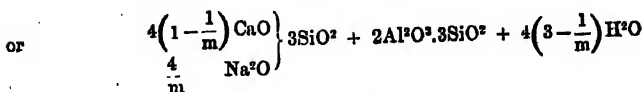
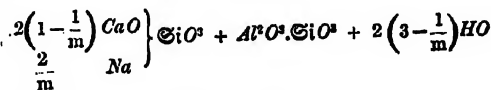
**MESOLITE.** The investigations of E. Schmid (*Pogg. Ann.* cxlii. 118) tend to show that this mineral is a distinct species, and not a variety of scolécite, as supposed by Rammelsberg (v. 207). Schmid examined three specimens, two from Iceland (I. and II.), the former consisting of radiated bundles terminating in free crystals, which exhibit the combination of the monoclinic prism with the clin-

pinacoid and the complete pyramid, while the latter and that from Stromb (III.) are finely radiate, the ends not being free. At ordinary temperatures they lose but little water, probably hygroscopic, the quantity not being greatly increased when the heat is raised to 100°. Above the boiling point the loss increases, and by a gentle incandescence continued for half a hour, all the water of the three specimens, amounting to 12.943, 13.190, and 13.355 p.c. respectively, was driven off. Coarse fragments, after lying two days in acid, show signs of gelatinisation. The portions analysed were dried at 100°, and had consequently lost somewhat more than the hygroscopic water; the results were:—

	I.			II.			III.		
		Oxygen	Oxygen ratios		Oxygen	Oxygen ratios		Oxygen	Oxygen ratios
Silicic acid	46.583	24.842	5.802	47.133	25.136	6.102	47.404	25.231	6.107
Alumina, with a trace of iron oxide	27.566	12.845	3.00	26.520	12.358	3.00	27.049	12.605	3.00
Lime	9.105	2.602	0.836	10.365	2.961	1.006	9.163	2.618	0.919
Magnesia	0.076	0.030		0.025	0.00		0.058	0.023	
Soda	3.638	0.948		4.501	1.173		4.689	1.222	
Specific gravity	2.18	—	—	2.18	—	—	2.16	—	—

The ratios of the constituents, with the exception of the water, are those of labradorite. The amounts of water in these three new specimens show as little uniformity as those of earlier analyses, and it is this point, in fact, that has made the recognition of mesolite as a distinct mineral species a matter of doubt. Fuchs held that the water-percentage was dependent on those of soda and lime, and considered mesolite to be formed of scolecite and natrolite as proximate constituents. If then the oxygen of the soda be  $\frac{1}{m}$  of that of the total monoxides, the water will, on this assumption, be

$3 - \frac{1}{m}$ , and the formula:—



**METALDEHYDE.** See ALDEHYDE.

**METALS.** On the Atomic Weights and Classification of the Metals, see ELEMENTS (p. 462).

On the Electric Effects produced by the Contact of Metals with Water, Acids, and Saline Solutions, see ELECTRICITY (pp. 443–446). On the Thermo-electric Actions of Metals and Liquids (p. 457).

On the Colours of Metals, see LIGHT (p. 746).

On the Solution of Metals in Liquid Ammonia, and on the supposed Metal-ammoniums, see AMMONIA (p. 60).

**Distinction of Base from Noble Metals.**—According to P. Guyot (*Zeitschr. anal. Chem.* ix. 516), a solution of auric chloride or silver nitrate produces on alloys containing base metals, brown or grey spots, whereas on pure gold or on articles gilt therewith, this effect is not produced. Lustres on tapestry or paper-hangings may be tested with *sulphur chloride*, a drop of which placed on impure lustre immediately produces a brown rim, which is not the case when the coating is of pure gold. Thin leaves of metal may be tested with *sulphur chloride* or with a solution of *phosphorus* in carbon sulphide. Aluminium immersed in such a solution remains bright for several months; silver turns brown, and platinum acquires a very faint golden lustre.

**Separation of Metals by Electrolysis.**—By employing an electric current of suitable intensity, it is possible to separate directly the more easily reducible metals from those

which are less reducible, and to obtain in this manner two distinct groups; the first comprising iron, nickel, cobalt, and zinc; the second, all the other metals capable of reduction, the latter group also representing those metals which are precipitable by a plate of zinc.

In the electrolytic separation of two metals (copper and cadmium, for example), differing but slightly in reducibility, it is found advantageous to employ a current somewhat stronger than would be necessary, supposing it were intended to avoid the precipitation of the less reducible metal. In this way a deposit is in the first instance obtained, containing the whole of the more reducible metal, together with a small quantity of the other metal; the solution is then poured off, replaced by a liquor free from metallic salts, and the direction of the current reversed for a short time. As soon as the deposited metals have passed into solution, the original direction of the current is re-established. The less reducible metal, being now only in very small proportion, remains entirely in solution, while the metal which is more easily reduced is deposited perfectly pure. It is sometimes, though not often, necessary to repeat this operation.

When a solution of cobalt, nickel, or zinc is reduced by galvanic action, it is advisable to superaturate the solution with ammonia, to avoid the deposition of oxide. It is found impossible to estimate iron correctly by the above method, owing to the great tendency of the metal to form sesquioxide (Lecoq de Boisbaudran, *Compt. rend.* lxxiii. 1322).

On the Electrolytic Separation of Copper and other Metals, as practised at the Mansfield Copper Mines, see COPPER (p. 384).

On the Action of Sulphurous Acid on Metals, see SULPHUROUS ACID.

On the Influence of certain Liquids in Retarding the Action of Acids on Metals, see CHEMICAL ACTION (p. 306).

**METAMORPHISM.** On the metamorphism of rocks, as exhibited in the contact phenomena produced between the clay-slates and granular diabases in the Harz, see E. Kayser (*Zeitschr. geolog. Gesellsch.* xxii. 103; *Jahrb. f. Mineralogie*, 1870, 496; *Jahresh. f. Chemie*, 1870, 1344).

An elaborate Treatise, of historico-critical character, on the Theory of Metamorphism and the Origin of Crystalline Slates, has been published by J. Roth (*Abhandl. d. Berl. Acad.* 1871, *physikalische Classe*, 151; *Verh. geol. Reichsanstalt.* 1871, 362).

On the Metamorphism of Meteorites, see p. 793.

**METATHIOHYDROBENZOIC ACID.** See TRITHIOHYDROBENZOIC ACID.

**METEORITES.** *Formation.*—Daubrée (*Compt. rend.* lxii. 200, 369, 666) has made a series of synthetical experiments with the view of throwing light on the mode of formation of meteorites, and on their relation to terrestrial rocks. He finds that ordinary meteorites (chondrites), when exposed in a plumbago crucible to a heat near the melting point of platinum, yield an iron regulus (proceeding partly from the metallic iron present, partly from reduction of ferrous silicate), together with a flux which on cooling solidifies to a crystalline mass containing two different crystallised bodies in very different proportions. The upper layer of this flux consists of olivine either in flat rhombic octohedrons, or in six-sided tables ( $OP \cdot \infty P\infty \cdot \infty P2$ ), or in laminae ( $OP \cdot P\infty \cdot nP\infty$ ). The inner mass consists of enstatite ( $MgO.SiO_2$ ) in prisms, not exactly definable, with rectangular base and fibrous-laminar fracture; sometimes the enstatite is intergrown with olivine or grouped more or less regularly round a nucleus of olivine. Meteorites of different groups (iii. 980) differ in their melting points only in consequence of the predominance of one or the other of these silicates. The Chassigny meteorite gave scarcely anything but olivine, that of Bishopville little besides snow-white enstatite; the aluminiferous meteorites of Jouvenas, Jousac, and Stannern, on the other hand, yielded glasses free from crystals; that from the Jouvenas meteorite was blistered. The enstatite and olivine, which exist in meteorites in a state of very intimate mixture, but may be shown to be present by their different behaviour to acids, crystallise therefore separately from the fused mixture, and enclose the alumina silicates in their mass, if the latter are not present in considerable quantity.

Exactly similar products are obtained by the fusion of terrestrial olivine rocks. Olivine melts completely in a strong gas-furnace, yielding a green translucent crystalline mass which exhibits well-defined crystals on its surface. Lherzolite melts still more readily, exhibiting after fusion distinct needles of enstatite, which occur more abundantly if silica has been added previously to the fusion. Serpentine yields by fusion and solidification crystals of olivine and enstatite; when fused with addition of magnesia, it is converted for the greater part into olivine; with addition of silica into enstatite. When these rocks are fused in a plumbago crucible, the result is essentially the same: the iron of the silicate is reduced and separated in the form of microscopic granules.

The reguline masses of iron obtained by the fusion of meteorites (which from their mode of formation probably contain carbon and silicon) sometimes exhibit on cut and polished faces, after treatment with acids, a dendritically ramified crystalline substance distinct from the dull ground, and in the case of the Montrejean and Aumale meteorites, also distinct crystals of titanium nitrocyanide, but not the regular (Widmanstätten) figures characteristic of the unaltered meteorite. The meteoric iron of Caille (Dep. of Var) after refusion (imbedded in alumina) exhibited the same appearances, although it had become crystalline throughout its mass.

The synthetical preparation of meteoric iron was not quite successful. Soft iron fused with phosphorus, nickel, silicon, and iron sulphide, acquires a distinctly crystalline character and laminar fracture, without, however, exhibiting on the etched cut surfaces the lines and separations of meteoric iron. A product at least resembling meteoric iron was obtained by fusing soft iron (or pig iron) with 2 to 10 p.c. of iron phosphide: it showed on unetched cut surfaces the iron phosphide in shining lines (only less regularly disposed than in meteoric iron) and a black amorphous substance, which was separated somewhat uniformly through the mass, and appeared also to consist of iron phosphide. A still better result was obtained by fusing 1800 grams of soft iron, 170 nickel, 50 iron phosphide, 40 iron monosulphide, and 20 cast iron rich in silicon. An iron containing iron phosphide and nickel, and similar in structure and composition to meteoric iron, separated on fusing olivin, hercynite, hypersthene, basalt, melaphyre, and serpentine in a plumbago crucible; any chromium present in these minerals also passed into the regulus.

Daubrée has also studied the analogies which exist between meteorites and rocks of the olivin family, and show themselves most distinctly in the structure of the fused rock. These rocks, like the meteorites, exhibit indications of cleavage-planes in the form of fine, sharply-drawn straight lines between irregular furrows; they also, like the meteorites, exhibit needles of enstatite; they have partly the granular consistence of the chondrites, and if they have been fused in a plumbago crucible, they assume, when two pieces are rubbed together, the same graphitic lustre that meteorites exhibit on friction surfaces, due in fact to the triturated powder of the imbedded metallic iron. The essential difference between the two consists in this, that in the terrestrial rocks all the constituents are combined with oxygen, whereas in the meteorites some of the constituents are present in the unoxidised state.

From all these facts Daubrée infers that meteorites have been brought to the state in which they fall to the earth, either by partial reduction of a rock of the olivin family, or by partial oxidation of metallic and metalloidal elements of the same rock, not originally combined with oxygen. He has tested the admissibility of both these hypotheses—of which he seems to prefer the second—by further synthetical experiments. When olivin, hercynite, or pyroxene, is heated to redness in a stream of hydrogen, the ferrous oxide contained in it is reduced, and the ferric phosphate is converted into iron phosphide. As meteorites, for the most part, do not contain carbon, it appears most probable that any reduction that may have taken place is due to hydrogen; the water resulting from it might, in consequence of the small size of the fragments, be volatilised. In corroboration of the second hypothesis the following experiments are adduced. Silicide of iron, imbedded in magnesia, and exposed for a quarter of an hour in an imperfectly closed crucible to the heat of a powerful gas-furnace, yielded granules of soft iron retaining only traces of silicon, and a fused magnesio-ferrous silicate, in the cavities of which octohedral crystals of olivin could be recognised. A mixture of 10 parts nickeliferous iron (containing 9 p.c. nickel), 1 part iron phosphide, 1 part iron monosulphide, 43 parts silica, and 57 parts magnesia, gave, when treated in like manner, a ferruginous olivin (free from nickel and phosphorus), partly crystallised in tables, and a regulus in which the sulphur and phosphorus of the mixture were concentrated (the phosphorus as phosphide of magnesium, nickel, and iron).

According to both the preceding hypotheses, the original material of the earth and the planetary bodies which have yielded the meteorites must have been the same, and the olivin rocks, which differ so remarkably from the rest in their basic character and their high specific gravity (up to 3.3), and, according to Daubrée's hypothesis, constitute, at certain depths, the chief constituent of the interior of the earth, must be regarded as the universal slag of the planetary system. In whatever way meteorites may have attained their present condition, their confused crystallisation and the irregular form of the iron-granules contained in them, tend to show that the temperature at which the changes in question took place could not have exceeded the welding heat of iron. In a mixture of hercynite and reduced iron fused at a high temperature, Daubrée found the separate iron-granules completely rounded.

The following observations throw further light on the structure of meteorites. When a polished plate of the meteoric iron of Charcas or Caille is immersed in a solution of



cupric sulphate, there is first formed on the white ground a copper-coloured network of Schreibersite needles, and immediately afterwards each needle becomes surrounded with a ring or aureole of copper, sharply defined on the inner as well as on the outer side. Scarcely have rings formed when the free parts of the surface likewise become coated with copper. This latter deposit cannot be rubbed off, but it may be removed by treatment with ammonia, and the surface of the meteoric iron then shows (still more distinctly if the deposition of the copper be interrupted at the moment when the rings appear, and the excess of the copper salt be removed by washing with a large quantity of water) a structure essentially different from the Widmanstätt figures, and designated by Daubrée as the primary network (*réseau de départ*). The long parallel brilliant needles of schreibersite, surrounded by the ring, may be distinguished on the grey fine-grained ground mass (Daubrée, *Compt. rend.* lxiv. 685).

To determine whether, in a meteoric stone containing both silicates and metallic portions, the iron is present as a coherent mass or in isolated grains, a fragment of the stone heated to redness may be quenched in cold water (or, to prevent oxidation of the metal) under mercury. In this manner Daubrée has found that the iron in the meteorite of Sierra de Chaco is in separate grains, whereas that of Atacama forms a coherent mass intersected by granules of silicate. In the meteorite of Rittersgrün, on the other hand, both the silicate and the iron are coherent masses intergrown with one another (*Compt. rend.* lxvi. 148).

**Classification.**—Rammelsberg classifies the constituents of meteorites as follows:—

1. *Metallic bodies*: Nickel-iron; schreibersite.
2. *Metallic sulphides*: Oldhamite,  $\text{CaS}$ ; troilite,  $\text{FeS}$ ; magnetic pyrites,  $\text{FeS}^2$ .
3. *Oxides*: Magnetic iron oxide,  $\text{Fe}^2\text{O}^3$ ; chromo-iron oxide,  $\text{FeCr}^2\text{O}^4$ .
4. *Silicates*; a. *Bisilicates or Metasilicates*: Enstatite,  $\text{MgSiO}^2$ ; bronzite,  $(\text{Mg}; \text{Fe})\text{SiO}^2$ ; augite  $(\text{Mg}; \text{Ca})\text{SiO}^2$ ; and  $(\text{Fe}; \text{Mg}; \text{Ca})\text{SiO}^2$ . b. *Singulosilicates or Orthosilicates*: Olivin,  $(\text{Mg}; \text{Fe})\text{SiO}^2$ ; anorthite,  $\text{CaAl}^2\text{Si}^2\text{O}^8$ .

To these must be added crystallised silica (tridymite?) and carbon, partly combined partly in the form of graphite.

Among the augitic or rhombic bisilicates of meteorites, Rammelsberg further distinguishes  $\text{MgSiO}^2$  as enstatite,  $n\text{MgSiO}^2 + \text{FeSiO}^2$  as bronzite when  $n > 3$ , and as hypersthene when  $n < 3$  (independently of admixtures of  $\text{R}^2\text{O}^3$  common to all the three types), and he infers, from a discussion of all the available analyses, that enstatite is contained in the meteorites of Bishopville, Rusti, and Deesa; bronzite in those of Breitenbach, Rittersgrün, Steinbach, and Shalka; non-ferruginous augite in the Rusti stone; ferruginous augite in those of Jouvenas, Stannorn, and Petersburg in Tennessee (*Pogg. Ann.* cxl. 311).

A comprehensive memoir on meteorites and their relation to terrestrial rocks has been published by S. Meunier (*Mouiteur Scientifique* [3], i. 97). He classifies meteorites under forty-three types, the names of which are formed from those of the respective localities with the suffix 'ite.' Many of these individual types exhibit a genetic connection; thus 'Decsite' (from Deesa in Chile) consists of a metallic ground-mass of 'caillite,' enclosing fragments of a mineral identical with 'tadjjerite' (the stone which fell at Tadjera, near Selif, in 1867). Further, though the metallic part of decsite is chemically identical with that of caillite, it is distinguished from the latter by the irregularity of its Widmanstätt figures, a property which may be imparted to caillite by refusion. By less strong heating, aumalite and chantonnite (iii. 980) may be converted into tadjjerite; on the other hand, the black crust of chantonnite consists of tadjjerite, a result which Meunier regards as related to the heat of friction developed in eruption.

From the comparison of a large number of examples, Meunier classifies his types as follows:—

1. *Stratiform meteorites* (caillite).
2. *Eruptive meteorites* (chantonnite); to which, also, belong the eruptive breccias (decite).
3. *Metamorphic meteorites* (tadjjerite).
4. *Brecciform non-eruptive meteorites* (meteorite of St. Mesmin).

With regard to the analogies between meteorites and terrestrial rocks, Meunier refers serpentine to chantonnite and aumalite, and explains the microscopical identity and chemical resemblance of the three bodies on the supposition that chantonnite is aumalite slightly metamorphosed (by the heat of friction of the eruption), and that serpentine is chantonnite, strongly oxidised and hydrated, forming the outcrop of the veins, just as malachite forms that of veins of copper pyrites. In short, he regards meteorites as the deeper-seated rocks of a star perfectly analogous in structure to the earth.

For Meunier's speculations on the successive transitions of a star from its originally

fluid state to a condition similar to that of the earth, afterwards to that of the moon, and its ultimate resolution into fragments like meteoric stones, we must refer to the original paper; see also *Jahresb. f. Chem.* 1871, 1235.

On the Metamorphosis of Meteorites, see further, Meunier (*Compt. rend.* lxxii. 452, 508, 541; *Chem. Soc. J.* [2], ix. 329 and 503-505).

*General Properties and Proximate Constituents of Meteoric Iron.*—Meunier (*Ann. Chim. Phys.* [4], xvi. 19) distinguishes the following varieties of nickel-iron:—

1. *Octibbehlite*,  $\text{FeNi}_2$ , of sp. gr. 6·854, constituting the entire mass of the meteoric iron of Octibbeha County, Mississippi.

2. *Tenite*,  $\text{Fe}^{\text{Ni}}$ , sp. gr. 7·380, containing 85 p.c. iron, 14·0 nickel, and a trace of cobalt; from the meteoric iron of Caille (*Alpes maritimes*).

3. *Plessite*,  $\text{Fe}^{10}\text{Ni}$ , sp. gr. 7·850 (origin not stated).

4. *Kamacite*,  $\text{Fe}^{14}\text{Ni}$ , sp. gr. 7·652, containing 91·9 p.c. iron, 7·0 nickel, and a trace of cobalt; from the meteoric iron of Caille. Also containing 92·0 iron, and 7·5 nickel from that of Charcas, in Mexico.

Of iron carbide, Meunier distinguishes two varieties, viz.: *Chalybite*,  $\text{CFe}_2$ , from the meteoric iron of Naakornak in Greenland; and *Campbellite*, with less carbon (1·50 p.c.), from that of Campbell County, Tennessee.

To *Troilite* Meunier assigns, contrary to ordinary acceptation, the formula  $(\text{Fe}; \text{Ni})\text{S}^{\text{S}}$ , basing his conclusion on the following analysis:—

	Fe	Ni	Cu	S
a. . . .	59·01	0·14	trace	40·03 = 99·18
b. . . .	56·29	3·10	—	39·21 = 98·60

a. From the meteoric iron of Toluca; b. from that of Charcas.

For *Schreibersite* he gives the formula  $\text{Fe}^{\text{Ni}}\text{P}$ , deduced from an analysis of schreibersite from the Toluca iron:—

Fe	Ni	Co	Mg	P	Sp. gr.
57·11	28·35	trace	trace	15·01 = 100·47	7·103

In two graphites Meunier found:—

	C	Fe	Ni	Sp. gr.
a. . . .	97·3	2·4	trace = 99·7	1·715
b. . . .	98·0	0·9	— = 99·0	1·309

a. From the meteoric iron of Caille; b. from that of Charcas.

The crust of the Toluca iron was found to consist of—

$\text{Fe}_2\text{O}_3$	FeO	NiO	CoO	Sp. gr.
68·93	28·12	2·000	trace = 99·05	4·89

whence it appears to consist of nickeliferous magnetic iron oxide.

The non-metallic granules are distinguished as those which belong to the metallic iron and those which belong to the troilite. Both kinds are indistinctly crystallised, the former from the iron of Tucson, in Mexico, have a sp. gr. of 3·35, and contain silica, ferric oxide, and magnesia. Meunier regards them as hyalosiderite. In the grains from the Caille and Charcas irons he found only silica, and inclines to the opinion that they consist of quartz.

With respect to the gases enclosed in meteoric iron, Meunier was unable to find anything but atmospheric air, whereas Graham found hydrogen in the meteoric iron of Lenarto (1st Suppl. 635). Graham, however, remarks that, as Meunier made use of mercuric chloride to dissolve the iron, the hydrogen, from its metallic nature, would give rise to a precipitation of mercury without evolution of hydrogen, and therefore that Meunier's result cannot be regarded as conclusive against the existence of hydrogen in the meteoric iron.

The Widmanstätt figures are attributed by Meunier, not to schreibersite, but to troilite, inasmuch as they are developed by the action of fused potash as well as by that of acids, whereas schreibersite is attacked by melting potash.

Meunier classifies meteoric irons according to the predominance of one or more varieties of nickel-iron contained in them; thus:—

I. Meteoric-iron consisting exclusively or for the most part of one nickel-iron; viz.:—

1. *Octibbehlite*,  $\text{FeNi}_2$ , from Octibbeha.

2. *Tenite*,  $\text{Fe}^{\text{Ni}}$ , from Tazewell.

3. *Kamacite*,  $\text{Fe}^{14}\text{Ni}$ , from Nelson.

II. Mixtures of two nickel-irons:—

4. *Tenite* and *Kamacite*, from Caille.

5. *Tenite* and *Plessite*, from Jewell hill.

6. *Tenite* and *Campbellite*, from Campbell County.

## III. Mixtures of three nickel-irons:—

7. *Tenite*, *Kamacite*, and *Plessite*, from Burlington.

Rammelsberg (*Zeitschr. geolog. Ges.* xxii. 893; *Jahresb. f. Chem.* 1870, 1395) objects to Meunier's conclusion that the iron sulphide of meteorites consists of magnetic pyrites,  $\text{FeS}^8$ . By a renewed analysis of troïlite from the meteoric iron of Seelsgen, he obtained:—

P	Fe	Ni <sup>8</sup>	S
0.18	62.24	1.00	35.68 = 100.

Deducting the nickel and phosphorus, together with the corresponding quantity of iron, as schreibersite, there remains for the iron sulphide 61.97 p.c. iron to 38.03 sulphur, giving the atomic proportion of  $\text{Fe} : \text{S} = 100 : 107$ , instead of  $100 : 100$ . Nevertheless Rammelsberg is inclined, according to the analogy of the older analyses, to admit the formula  $\text{FeS}$ ; and the more so as he regards Meunier's method of analysis, which led to the formula  $\text{FeS}^8$ , as inadmissible.

J. L. Smith (*Sill. Am. J.* [2], xlix. 331) directs attention to the general occurrence of cobalt and copper in meteoric iron, and is inclined to regard both these elements as essential constituents of it. Tin he has never found; lead only in the Tarapaca iron, its occurrence in which is also mentioned by Greg (*Jahresb. f. Chem.* 1855, 1027). Smith is, however, of opinion that the presence of the lead must be attributed to fusion-experiments which had been made with this iron with the view of obtaining noble metals from it. Pieces from the interior, free from cracks, contained no lead.

The composition and physical character of the meteorites which had been most exactly investigated down to the year 1859, are given in vol. iii. pp. 977–982. To describe the large number which have been examined since that date would take up more space than can be devoted to the subject in this volume (see *Jahresb. f. Chem.* 1860–1871). The following have been recently examined:—

**Meteoric iron.**—1. J. W. Mallet (*Sill. Am. J.* [3], ii. 200) describes three masses of meteoric iron found in Augusta County, Virginia, weighing 56, 36, and  $3\frac{1}{2}$  lbs.

All three specimens presented the same general appearance. They were of a very irregular pear shape, one end of each mass being larger and more rounded than the other. On the exterior they were covered with a dark brown crust, consisting essentially of hydrated ferric oxide, which varied from about one-eighth to one-third of an inch in thickness. The masses were of course magnetic, and on examination gave evidence of feeble magnetic polarity, with multiple poles. The interior structure of the iron was compact, and highly crystalline, of much the same general character throughout; but a few small grains and streaks of a brownish-yellow mineral were noticed, which on being picked out and examined, proved to be *troïlite*. Minute fissures also were observed running through several portions of the metal, from which a watery liquid containing chlorine exuded. Traces of Widmanstätten figures might be detected upon a polished surface, even without the aid of an acid; and when the iron had been etched with nitric acid, the markings became very distinct and beautiful. In all three specimens, upon the principal cut surfaces, narrow, well defined bands of alternate nickel-iron and schreibersite were visible, the alternations sometimes running parallel, but more often intersecting each other at angles of  $60^\circ$ ,  $90^\circ$ , or  $120^\circ$ .

The iron was not passive, but very easily rendered so by nitric acid.

The following are the results of analysis, No. 1 representing the largest, and No. 3 the smallest specimen:—

	No. 1	No. 2	No. 3
Specific gravity at $15^\circ \text{C.}$ . . . .	7.853	7.856	7.839
Iron . . . . .	88.706	88.365	89.007
Nickel . . . . .	10.163	10.242	9.964
Cobalt . . . . .	.396	.428	.387
Copper . . . . .	.003	.004	.003
Tin . . . . .	.002	.002	.003
Manganese . . . . .	trace	—	trace
Phosphorus . . . . .	.341	.362	.375
Sulphur . . . . .	.019	.008	.026
Chlorine . . . . .	.003	.002	.004
Carbon . . . . .	.172	.185	.122
Silica . . . . .	.067	.061	.066
	99.872	99.659	99.947

Each specimen contained a small quantity of tin, a metal which has been said seldom or never to accompany meteoric iron. The chlorine is probably not an essential constituent of the original masses, but has been derived from the soil in which the iron has lain imbedded. No chlorine could be detected in a specially selected solid piece, of some 50 grams weight, taken from a part of No. 1 destitute of fissures and flaws.

The siliceous residue, although returned as silicic acid, appeared upon examination to have existed partly in combination as silicide of iron.

Cuttings of this iron, heated in a porcelain tube connected with a Sprengel pump, gave off gas having the following composition:—

H	CO	CO <sup>2</sup>	N
35.83	38.33	9.75	16.09 = 100

124.59 grams of the iron having a volume of 15.87 c.c. yielded 36.33 c.c. of gas at 0° C. and 760 mm. in 14½ hours, the greater portion being given off in the first 2½ hours.

The proportion of hydrogen in the Virginia iron is much less than in that of Lenarto analysed by Graham (1st Suppl. 635), and that of carbon monoxide much greater. Graham's analysis of the Lenarto iron shows no carbon dioxide (Mallet, *Proc. Roy. Soc.* xx. 365).

2. *Meteoric iron from Trenton*, Washington Co., Wisconsin, has been analysed by J. L. Smith (*Jahresb. f. Min.* 1871, 178), and from the desert of Atacama by E. Ludwig (*Wien. Acad. Ber.* lxiii. [2], 323)—

	Fe	Ni	Co	Cu	P	Insoluble	
Wisconsin	91.03	7.20	0.53	trace	0.14	0.45	= 99.35
Atacama	91.53	7.14	0.41	trace	0.45	—	= 99.53

The Wisconsin iron is in several masses, the largest of which is 14 inches long, 8 inches broad, 4 inches thick, and weighs 62 lbs. Sp. gr. = 7.82. The Atacama specimens are polished on the surface, quite free from oxide, and dissolve without residue in warm nitric acid. One of the smaller fragments was found to contain a very small quantity of sulphur.

3. C. U. Shepard (*Sill. Am. J.* [3], iii. 438) describes meteoric iron from El Dorado Co., California. The mass, weighing 85 lbs., was found in a field; its surface shows the indentations common to these bodies, the crust or coating being slightly oxidised. Turnings taken from it exhibit a sp. gr. of 7.80, which is perhaps a little above that of the mass.

The fragments examined were free from sulphur. A single analysis made on a gram of material gave 88.02 p.c. iron, 8.88 nickel, and 3.50 insoluble matter consisting of a mixture of ferrous and ferric oxides, with many silvery particles of supposed metallic phosphides (schreibersite).

4. *Meteoric Iron from Greenland*.—This iron, described by Nordenskiöld (*Deut. Chem. Ges. Ber.* iv. 987), was found by the Swedish expedition of 1871 on the sea-shore at Oviak near Disco Bay, at the foot of a basalt mountain, in three masses, weighing 300, 200, and 100 centners, together with several smaller pieces. It is very hard, crystalline, and brittle, but when moved to a warmer climate, weathers very rapidly and crumbles to a coarse-grained powder.

Metallic iron is also found in the solid basalt near the locality of the loose blocks, and on the other hand many of these loose masses are partly encrusted with rock of the same character as the neighbouring basalt, a circumstance which seems to indicate that the loose blocks also originally belonged to the basalt. The composition of the loose and imbedded masses is likewise consistent with the supposition of a community of origin, as the following analyses will show:—

a. One of the larger blocks, analysed by Nordenskiöld; b. One of the smaller loose masses, analysed by Nordström; c. Iron from a vein in the basalt, analysed by Lindström.

All the three samples contain nickel. The unusually large, though varying amount of carbon is also common to them all; so likewise is the considerable proportion of chlorine, which shows itself during the weathering of the iron by the exudation of watery drops of iron chloride. The Widmanstätt and Setven figures are most distinct in the iron from the basalt.

	<i>a</i>	<i>b</i>	<i>c</i>
Iron . . . . .	81.40	86.34	93.24
Nickel . . . . .	2.48	1.64	1.24
Cobalt . . . . .	0.07	0.35	0.56
Copper . . . . .	0.27	0.19	0.19
Alumina . . . . .	trace	0.24	—
Limo . . . . .	—	0.48	—
Magnesia . . . . .	0.04	0.29	trace
Potash . . . . .	trace	0.07	0.08
Soda . . . . .	—	0.14	0.12
Phosphorus . . . . .	0.20	0.07	0.03
Sulphur . . . . .	1.52	0.22	1.21
Chlorine . . . . .	0.72	1.16	0.16
Silica . . . . .	trace	6.66	0.59
" undissolved . . . . .	0.05	4.37	—
Carbon, organic matters, } oxygen, and loss . }	10.16	3.71	{ C 2.30 H 0.07
	100.00	105.93	99.70

From this community of character it might perhaps be inferred that the whole consists of native metallic iron. The discoverer, however, is more inclined to regard it as due to a fall of meteorites at a very remote epoch, before the volcanic ashes had hardened into the existing basalt. The decided meteoric shape of the masses, their porosity, and the presence of organic matter—circumstances which cannot well be reconciled with the supposition that the iron has been ejected from the interior of the earth in a state of igneous fusion—together with the presence of nickel, &c., all afford evidence of meteoric origin (Nordenskiöld).

Near the large iron masses above described other iron was found in grains and spherular masses; also a vein of the metal several inches wide and some feet in length, enclosed in a rock which is apparently trap, but shows a marked difference in composition from the basalt-breccia from which it protrudes. The metal of this vein, which has been examined by Wöhler (*Ann. Ch. Pharm.* clxii. 247), resembles grey cast iron; it has a bright lustre, is very hard, quite unalterable in air, and has a specific gravity of 5.82. Nordenskiöld obtained gas from the metal of the larger masses by heating them; Wöhler finds that the iron of the vein evolves more than 100 times its volume of a gas which burns with a pale blue flame, and consists of carbon monoxide mixed with a little dioxide. The 'iron,' in fact, contains a considerable amount of carbon and a compound of oxygen, and has evidently not been at any time exposed to a high temperature. By heating, the iron becomes brighter in appearance, and though more soluble in acid, still leaves a carbonaceous residue. A fragment heated in hydrogen lost however 11.09 p.c., or, in other words, was shown to contain that amount of oxygen. Hydrochloric acid acts but slowly and partially on this metal, evolving sulphuretted hydrogen and then hydrogen having the odour of a hydrocarbon, and leaves a black granular magnetic powder which, though insoluble in acid when cold, generates, on the application of heat, a gas with a strong odour of a hydrocarbon, and leaves a residue of amorphous sooty carbon and slightly lustrous graphitic particles. In ferric chloride the 'iron' dissolves without evolution of gas, leaving about 30 p.c. of a black residue which, after having been dried at 200°, loses by subsequent ignition in hydrogen 19 p.c. of its weight, water being formed. This residue is very readily attacked by acid, evolves sulphuretted hydrogen, and leaves a nearly pure carbon in powder and graphitic scales. Ferric chloride and hydrogen chloride appear, therefore, to remove the free metal only, and to be without action on its compounds with sulphur and oxygen. The 'iron' has the following ultimate composition:—

Iron	Nickel	Cobalt	Phosphorus	Sulphur	Carbon	Oxygen	
80.64	1.19	0.49	0.15	2.82	3.69	11.09	= 100.07

The oxygen which constitutes so considerable a part of an apparently metallic mass might be regarded as present in the form of a differrous oxide,  $\text{Fe}^{\text{O}}$ , were it not that this view provides no iron for combination with sulphur and carbon. As Nordenskiöld found magnetite,  $\text{Fe}^{\text{O}}$ , in other Ovifak irons, Wöhler regards the iron compound which constitutes the veins as an intimate mixture of magnetite, of which there would be 40.2 p.c., with metallic iron, its sulphide, carbide, and phosphide, its alloys with nickel and cobalt, and some carbon in isolated particles. The latter undergoes no change when the magnetite and carbide, by the action of heat, generate carbonic oxide.

**Meteorite Stones.** 1. *The Hesse Meteorites.* A remarkable fall of meteoric stones, which took place on January 1, 1860, at Aerno near Hesse on the Mälar Lake, in Sweden, is recorded by Haidinger (*Wien. Acad. Ber.* lix. [2], 224). These stones, some of which were twice the size of the fist, were spread over a tract of country 16 km. long and 5 km. broad. They have been analysed by A. E. Nordenskiöld (*Pogg. Ann.* cxli. 205). Their weight varies from 0.07 gram to 1791 grams, and their specific gravity from 3.671 to 4.004. Some of them which fell on ice or snow crumbled to a black-brown powder, which contained, together with a few magnetic particles, 4.3 p.c. water (at 110°) and glowed when heated, giving off a small quantity of a brown distillation-product and leaving a red-brown powder. The analysis of this powder gave, together with traces of lithia—

C	H	O	SiO <sup>2</sup>	FeO	MgO	CaO	Na <sup>2</sup> O	
51.6	3.8	16.7	16.7	8.4	1.5	0.8	1.5	= 100

These stones are encrusted, black on the outside, grey within, porous, and adhere to the tongue. They are composed of silicates and metallic grains bound together by a whitish-grey porous mass.

(1.) *Total Analysis.*—*a* (Lindström). Stone from Hesse; *b* and *c* (Nordenskiöld). *b* found in the ice between Arnö and Hesse, *c* at Arnö.

(2.) Silicate of 1*a*, analysed by Lindström: *a*. After digestion with mercuric chloride. *b*. After separation of the magnetic particles.

(3.) Nickel-iron. *a*. The portion dissolved in mercuric chloride from analysis 1, after deduction of a portion of iron which binds the S to FeS (Lindström). *b* from 1*b*; *c* from 1*c* (Nordenskiöld). The analyses lead to the formula Fe<sup>8</sup>Ni.

(4.) Portion of the silicate of 1*a*, which is soluble in strong hydrochloric acid; 48.67 p.c. of the total quantity of silicate after deduction of FeS (Lindström).

(5.) Insoluble portion after deduction of 1.90 p.c. chromiferous residue undecomposable by hydrofluoric acid (Lindström).

(6.) Analysis of the spherules which make up the chief mass of the Balingsta stone, after deduction of nickel-iron and ferrous sulphide (Nordenskiöld).

(7.) Powder of the stone obtained by pressure between the fingers and sifting through a thick cloth, after deduction of the magnetic particles and ferrous sulphide; *a* and *b*, total analysis; *c*, undissolved matter (42.8 p.c.); *d*, dissolved (56.2 p.c.) (Nordenskiöld).

The proximate constituents of the Hesse meteorites are, according to Nordenskiöld, 20 p.c. nickel-iron (Fe<sup>8</sup>Ni), small quantities of schreibersite, chrome-iron, troilite, and carbonaceous matter, 10 p.c. labradorite and anorthite, 37 p.c. olivin, and 23 p.c. shepardite, the last two not separately recognisable.

2. *Meteorite of Ibbenbüren, Westphalia.*—This meteorite fell on June 17, 1870. Its fall was witnessed by a peasant, who two days afterwards found it buried in a path-way, 27 inches below the surface. Before reaching the ground, one end of the stone had split off, and a fragment of the detached portion, weighing 30 grams, was found some 300 yards away.

The general form of the meteorite is that of a flattened spheroid. Its dimensions are: length, 0.125; breadth, 0.112; thickness, 0.093 meter; probable length before fracture, 0.180 meter. The exterior of the stone consists of a black layer, scarcely 0.1 mm. thick, which is not smooth and even, but covered with a number of extremely fine fused granulations. When examined with a magnifying glass, the surface exhibits innumerable branching cracks, which penetrate into the interior of the stone, and are filled with the fused mass of the exterior. Inside, the meteorite is much lighter in colour than meteorites generally. It consists of a greyish-white mass, interspersed with a very large number of irregularly distributed crystalline granules of a light yellowish-green colour, some imperceptibly small, others of considerable size, and mostly several millimeters in length. These crystals belong to the rhombic system, but it has not been found possible to determine their exact form. Their mean sp. gr. is 3.426. An analysis of them gave the following result:—

SiO <sup>2</sup>	FeO	MnO	MgO	CaO	Al <sup>2</sup> O <sup>3</sup>
54.51	17.53	0.29	28.43	1.04	1.26 = 101.06,

showing that the crystals are bronzite, with a large proportion of iron.

The mass of the meteorite, in which the crystals are embedded, is finely granular, white or light grey, and very brittle. Its sp. gr. is 3.404. Two analyses of it show that it is almost identical in composition with the crystals of bronzite contained in it.

The Ibbenbüren meteorite is remarkable for the simplicity of its constitution, consisting almost entirely of a single silicate, bronzite. It contains no chrome-iron ore, which is almost always present in meteorites, and no trace of any sulphur-compound. Traces of metallic iron, however, appear to be present. The surface is distinctly attracted by the magnet, a portion of the ferrous oxide of the bronzite

# METEORITES.

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METEORITES OF HESSEL, IN SWEDEN.

	1			2			3			4	5	6	7			
	a	b	c	a	b	c	a	b	c				a	b	c	d
Silica . . . . .	36.83	36.75	37.08	48.21	50.97	—	—	—	—	41.40	60.06	47.55	44.24	44.23	57.54	38.92
Alumina . . . . .	2.38	2.00	1.11	3.11	3.04	—	—	—	—	0.06	5.86	2.41	3.48	3.60	2.92	4.12
Chromic oxide . . . . .	0.07	—	—	—	—	—	—	—	—	—	trace	—	—	—	—	—
Ferrous oxide . . . . .	10.85	13.36	13.49	14.16	12.59	—	—	—	—	17.13	8.29	17.09	15.42	17.11	10.19	22.50
Manganese oxide . . . . .	0.42	—	trace	0.55	—	—	—	—	—	—	—	trace	—	—	—	—
Magnesia . . . . .	23.21	26.06	24.06	30.38	28.74	—	—	—	—	38.72	19.28	29.22	31.19	29.84	21.13	36.61
Lime . . . . .	1.80	1.50	2.66	2.36	2.88	—	—	—	—	1.57	4.10	1.86	2.30	2.06	2.92	1.40
Soda* . . . . .	0.94	1.03*	2.11*	1.23	1.55	—	—	—	—	0.63	2.41	0.47	1.45	1.96	2.56*	1.45*
Nickel oxide . . . . .	—	—	—	—	0.10	—	—	—	—	0.21	—	trace	—	—	—	—
Nickel . . . . .	2.15	1.98	2.33	—	—	—	11.34	11.15	12.51	—	—	—	trace	trace	—	trace
Cobalt . . . . .	0.02	trace	trace	—	—	—	0.11	trace	trace	—	—	—	—	—	—	—
Iron . . . . .	20.08	16.42	16.29	—	—	—	88.23	88.55	87.29	—	—	—	—	—	—	—
Phosphorus . . . . .	0.15	trace	trace	—	—	—	0.32	—	—	trace	—	—	—	—	—	—
Sulphur . . . . .	1.88	0.37	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Chlorine . . . . .	0.04	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Stannic oxide . . . . .	0.02	0.01	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—
Cupric oxide . . . . .	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Carbon . . . . .	trace	trace	trace	—	—	—	—	—	—	—	—	—	—	—	—	—
Insoluble residuum . . . . .	—	0.52	0.85	—	—	—	—	—	—	—	—	0.52	1.68	1.20	2.74	trace
Totals . . . . .	100.84	100.00	100.00	100.00	99.87	99.80	100.00	100.00	99.80	99.72	100.00	99.12	99.76	100.00	100.00	100.00

\* With traces of lithia and potash.

having been converted into magnetic oxide by the combined action of the oxygen of the air and a high temperature. At present only three other meteorites of similar constitution are known: the Chassigny meteorite, consisting of olivin; the Bishopville, of enstatite; and that which fell at Manegaum, in Hindostan, in 1843, and consists, like the present, almost entirely of bronzite (G. vom Rath, *Pogg. Ann.* cxlvi. 463).

3. *Meteorite from Bandong, Java.*—This stone, weighing 2,240 grams, fell, with five others, on December 10, 1871. It is an irregular rounded fragment, of sp. gr. 3.519, with a dull blackish surface, presenting numerous spherical indentations. The fracture shows a pale grey stony matrix of silicates, in which are distinguished metallic grains of three different kinds. The first, of an iron-grey colour, consist of nickel-iron; others, of a bronze-yellow colour and iridescent, are iron sulphide; and a third kind, black and insoluble in hydrochloric acid, consists of chromic iron. Under the microscope a thin section of the matrix is crystalline and transparent.

Analysis gave the following results:—

*Soluble in Hydrochloric Acid, 60.17 p.c.*

S	Fe	Ni	Co	MnO	FeO	MgO	CaO	K <sup>2</sup> O	Na <sup>2</sup> O	Al <sup>2</sup> O <sup>3</sup>	SiO <sup>2</sup>
2.13	4.95	1.03	0.14	0.12	16.87	12.81	0.30	0.89	0.70	1.43	17.25 = 58.62

*Insoluble in Hydrochloric Acid, 39.83 p.c.*

Chromo-iron	MnO	Fe <sup>2</sup> O <sup>3</sup>	MgO	CaO	K <sup>2</sup> O	Na <sup>2</sup> O	Al <sup>2</sup> O <sup>3</sup>	SiO <sup>2</sup>
4.41	trace	4.30	0.43	0.76	0.18	1.49	2.53	20.40 = 39.50
								98.12

Hence the meteorite appears to consist of:—

Nickel-iron	Iron sulphide	Chromo-iron ore	Peridote	Augite	Felspathic mineral
2.81	5.44	4.41	47.26	20.98	17.00 = 97.90

(Daubrée, *Compt. rend.* lxxv. 1676).

4. *Meteorite of Lodran*, near Moulton in India: October 1, 1868. (G. Tschermak, *Pogg. Ann.* cxl. 321). This partially encrusted stone is a very distinct mixture of nickel-iron, olivin, bronzite, magnetic pyrites, and chromo-iron. The nickel-iron contains:

Fe	Ni	MgO	Residue
85.44	12.79	0.25	0.81 = 99.29

The olivin (A) and bronzite (B) have been examined crystallographically by V. v. Lang. The former, which is of a blue or bluish-grey colour, is fringed on its cracks with mineral dendrites, probably proceeding from chromo-iron, as indicated by the analysis. The olivin substance contains 82 p.c. magnesium silicate to 18 p.c. iron silicate. The green or yellow-green bronzite exhibits three kinds of microscopic imbedded crystals, besides capillary bodies, apparently consisting of felspar and chromo-iron. The composition answers to 78 p.c. magnesium silicate to 22 p.c. iron silicate.

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Cr <sup>2</sup> O <sup>3</sup>	FeO	MgO	CaO	
40.14	—	0.60	13.35	46.01	—	= 100.30
55.35	0.60	—	12.13	32.85	0.58	= 101.51

Sp. gr. of A = 3.307; of B = 3.313

The ferrous sulphide does not exhibit crystalline forms, but in the chromo-iron the forms O,  $\infty$ O and 3O3 are recognisable. An approximate estimation of the entire mass gave 32.5 p.c. nickel-iron, 28.9 olivin, 31.2 bronzite, with a little chromo-iron and anorthite (?) and 7.4 magnetic pyrites.

5. *Meteorite of Shalka, in Bengal.*—This meteorite, which fell on November 30, 1850, is, according to G. Rose (*Pogg. Ann.* cxxiv. 193), a fine-grained mixture of dark green olivin with a white silicate, and isolated granules of chromo-iron. It is coated with a dull blackish-brown crust. Rammelsberg (*ibid.* cxli. 276) finds that its powder may be separated by levigation into a lighter (A) and a heavier portion (B), and the former by the action of acid into a decomposable portion (a) and an undecomposable portion (b).

	SiO <sup>2</sup>	FeO	MgO	CaO	Na <sup>2</sup> O	Cr <sup>2</sup> O <sup>3</sup> , FeO	Insoluble
A. a	3.84	3.01	3.17	trace	—	2.11	86.43 = 99.46
b	55.55	16.53	77.73	0.09	0.92	0.33	— = 101.15
B.	52.25	20.02	25.96	1.03	—	0.73	— = 100



From these numbers the proximate constituents, independently of the chrome-iron, may be calculated as

	A	B
Bronzite . . . . .	83.67	83.9
Olivin . . . . .	11.33	16.1

This analysis confirms G. Rose's conclusion as to the existence of two silicates in the meteorite.

6. The meteorite of *Goalpara*, in Assam, of unknown date, has the appearance of a coarse-grained olivin, of dark grey colour, and consists of 8.49 p.c. metallic iron, 0.85 hydrocarbon, 61.72 olivin, and 30.01 onstatite (Techemak n. Teclu, *Wien. Akad. Ber.* lxii. [2], 852, 855).

7. The meteorite of *Dusti*, in India, contains globules of calcium sulphide and small golden-yellow octohedrons called osbornite, apparently consisting of an oxysulphide of titanium and calcium; these, together with the calcium sulphide, are imbedded in angite (Muskolyne n. Flight, *Proc. Roy. Soc.*)

8. The meteorite which fell at *Khetree*, Rajputana, has been analysed by D. Waldie (*Chem. News*, xxi. 278). It exhibits light and dark grey portions, partly arranged in layers, partly forming small spherules which are difficult to separate from one another. Sp. gr. 3.612-3.818. It consists of nickel-iron (A), troilite, FeS<sup>2</sup>, and schreibersite (B), soluble silicates (C), and insoluble silicates (D):—

	Fe	Ni	Co	Cr	S	P	
	16.98	1.26	0.21	0.10	—	—	= 18.55
	3.34	—	—	—	1.76	0.12	= 5.22
SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Cr <sup>2</sup> O <sup>3</sup>	FeO	MgO	CaO	Na <sup>2</sup> O	X <sup>*</sup>
10.73	0.41	—	7.51	13.76	0.68	0.09	2.00 = 35.18
24.44	1.36	0.40	3.65	10.04	1.69	0.78†	— = 42.36

101.31

9. A meteorite which fell in *Stewart Co., Georgia*, on October 6, 1869, has been examined by J. E. Willet (*Sill. Am. J.* [2], xl. 331). Its fall was accompanied by seven explosions, and the stone immediately after its fall was found buried to the depth of about a foot, and not sensibly hot. It was coated, excepting on a few small portions, with a black crust of the thickness of paper. It had the form of an irregular cone, and weighed about 365 grams. The surface, when freed from the black crust, was grey and studded with green spherules of fibrous structure, the fibres, however, radiating, not from the centre of the spherule, but from a point on its surface; between these were whitish grains, dark particles, and spots of chrome-iron. The chemical analysis by J. L. Smith showed that the stone consists of:—

Nickel-iron . . . . .	7.00	
Ferrous sulphide . . . . .	6.10	
Bronzite or hornblende	}	86.90
Olivin . . . . .		
Albite or oligoclase		
Chrome iron . . . . .		

The nickel-iron contains 86.02 p.c. Fe, 12.01 nickel, and 0.75 cobalt.

10. *Meteorite of Tjube, India*.—This meteorite fell on December 9, 1869. Nine hours after its fall it was still too hot to be touched by the hands. It weighed 10 kilograms and had a specific gravity of 3.496. A portion (14 p.c.) was separable by the magnet and had a specific gravity of 6.8 at 15°. The ratio of nickel to iron in the magnetic portion was 1 : 16. The siliceous portion gave by analysis:—

Matter insol. in HCl	Iron sulphide	SiO <sup>2</sup>	MgO	FeO	CaO	Na <sup>2</sup> O with trace of K <sup>2</sup> O	Al <sup>2</sup> O <sup>3</sup>	MnO	NiO
50.14	3.71	14.95	16.40	12.01	0.74	0.32	0.22	0.30	traces = 98.79

11. *Meteorite of Tadjera*.—This stone, which fell on June 6, 1867, at Tadjera, near Sétif in Algeria, contains, according to Meunier (*Ann. Ch. Phys.* [4], vii. 5), 54.64 p.c. decomposable silicates, 28.80 undecomposable silicates, 0.20 chrome-iron ore, 8.04 troilite, and 8.32 nickel-iron.

12. *Meteorites of Danville in Alabama*.—A number of stones fell in this locality at 5 p.m. on November 27, 1868. The one examined had the usual black crust, was of a grey colour on a freshly-broken surface, and somewhat oolitic in its structure. Troilite and nickeliferous iron were easily recognisable, and another mineral was observed

\* Loss by solution of separated silica.

† With traces of K<sup>2</sup>O.

which was probably enstatite. The specific gravity of the stone is 3.398. The iron has the following composition:—

Fe	Ni	Co	P	S
89.613	9.050	0.521	0.019	0.105 = 99.208

The troilite consists of 61.11 iron and 39.56 sulphur (= 100.67).

The stony portion of this meteorite is made up of 60.88 p.c. soluble, and 39.12 p.c. insoluble silicate, the latter being thus composed:—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	FeO	MgO	CaO
50.08	4.11	19.85	20.14	3.90 = 98.08

These numbers denote a mineral of the augite group. The analysis of the soluble portion (in which were found silica 45.90, magnesia 26.52, iron protoxide 23.64, alumina 1.78, and lime 2.31) yielded numbers corresponding with the constitution of an olivin (J. Lawrence Smith, *Jahrbuch. f. Mineralogie*, 1871, 82).

13. *The Franklin Meteorite*.—This stone fell four miles from Frankfort, in Franklin county, Alabama, on December 5, 1868. It weighed 1 lb. 9½ oz., and has a mean specific gravity = 3.31. It contains:—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Iron oxide	Chromium oxide	MgO	CaO	K <sup>a</sup> O	Na <sup>a</sup> O	S
51.33	8.05	13.70	0.42	17.59	7.03	0.22	0.45	0.23 = 98.02

with a trace of nickeliferous iron.

The chromium oxide corresponds with 0.62 p.c. chromite, the sulphur with 0.63 p.c. troilite. This stone belongs to the class to which G. Rose has given the name of *Howardite*, and resembles in its physical character the meteorite of Petersburg, Tennessee (G. J. Brush, *ibid.* 178).

14. *Meteorite of Searsport, Maine*.—The original mass of this meteoric stone would appear to have presented an oval sub-conical outline, the exterior being covered with a thick crust of at least one-sixteenth of an inch in thickness. Its colour is bluish-white, and remarkably uniform, but it is slightly stained in one or two places with ferric oxide. More than one-half of the meteorite is composed of small, rounded, translucent grains, vitreous in lustre, and rarely exceeding a mustard-seed in size. Between these, and often partially coating them, is a fine-grained white, or greyish-white mineral, which is supposed to be chladnite; it constitutes about one-fourth of the stone, is without visible crystalline structure, and rather loosely coherent. Minute points of bright meteoric iron are very thickly scattered throughout the mass, and a few grains of troilite are visible. In one spot only a peculiar blackish substance of small dimensions was noticed, which, on being touched with the point of a knife, was found to be soft, and to leave a bright metallic streak; it was probably a plumbaginous aggregate.

In appearance, especially in the well marked character of its granules, this stone closely resembles the Aussum (France) meteorite of December 1858, while in the thickness and general character of the crust it also corresponds with the celebrated Mauerkirchen stone of 1768.

It was analysed by J. L. Smith, with the following results: sp. gr. 3.701; stony matter, 85.38 p.c.; nickeliferous iron, 14.62 p.c. The iron yielded: iron, 90.02; nickel, 9.05; cobalt, 0.43. The stony portion, treated with a mixture of hydrochloric and nitric acids, gave: 52.3 p.c. soluble in acid, and 47.7 insoluble.

Both the soluble and insoluble portions consisted essentially of double silicates of iron and magnesium, the soluble part being classed as an olivin, while the insoluble was considered to be either bronzite or enstatite.

The proximate composition of the stone would therefore be:—

Nickeliferous iron	14.63
Magnetic pyrites	3.06
Olivin	43.04
Bronzite, with a little orthoclase and chrome-iron	39.27

(C. U. Shepard, *Sill. Am. J.* [3], 133, 200).

15. A meteorite which fell at *Adare*, in the county of Limerick, in 1810, has been analysed by R. A. Apjohn (*Chem. Soc. J.* [2], xii, 104). It consists of an earthy matrix in which are imbedded numerous small, shining, metallic particles. Its surface is dark-coloured and has a fused appearance. Sp. gr. = 3.94. Its proximate composition is:

Nickel-iron . . . . .	19.07
Magnetic pyrites . . . . .	6.54
Chrome-iron . . . . .	1.75
Soluble silicate . . . . .	35.44
Insoluble silicate . . . . .	37.07
	<hr/>
	99.87

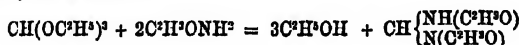
The metallic portion consists of 85.120 p.c. iron, 14.275 nickel, 0.602 cobalt, with a trace of phosphorus.

The composition of the soluble silicate (A) and insoluble silicate (B) is as follows:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	FeO	MnO	CaO	MgO	Na <sup>2</sup> O	K <sup>2</sup> O	P <sup>2</sup> O <sup>5</sup>
42.91	2.35	16.93	6.26	5.34	24.32	0.29	0.02	— = 98.42
59.48	3.24	7.94	8.84	4.62	13.17	1.86	0.30	trace = 99.45

This meteorite is especially interesting as containing also a small quantity of vanadium, affording indeed the first instance in which that element has been discovered in a meteoric stone.

**METHENYL-DIAMINES.** When orthoformic ether and acetamide are heated together in sealed tubes to 180°, cubic crystals are formed consisting of methenyl-diacetyl-diamine,  $\text{CH} \begin{Bmatrix} \text{NH}(\text{C}^2\text{H}^3\text{O}) \\ [\text{N}(\text{C}^2\text{H}^3\text{O})]'' \end{Bmatrix}$ , or  $\text{N}^2 \begin{Bmatrix} (\text{CH})'' \\ (\text{C}^2\text{H}^3\text{O})^2 \\ \text{H} \end{Bmatrix}$ . Their formation may be represented by the equation—



Besides these products, there are formed ethyl acetate and an amidomethenylimide,  $\text{CH} \begin{Bmatrix} \text{NH}^2 \\ (\text{NH}) \end{Bmatrix}$ , or methenyl-diamine  $\text{N}^2 \begin{Bmatrix} (\text{CH})'' \\ \text{H}^2 \end{Bmatrix}$ , which latter remains in solution, but has not yet been obtained in the free state. Its hydrochloride has the composition  $\text{CN}^2\text{H}^4.2\text{HCl}$ ; the platinumchloride is  $\text{CN}^2\text{H}^4.2\text{HCl.PtCl}^4$ . Methenyl-diacetyl-diamine heated with water is converted into the acetate of methenyl-diamine—



(Wichelhaus, *Deut. Chem. Ges. Ber.* iii. 2).

**METHYL ALCOHOL, CH<sup>3</sup>O.** On the formation of methyl alcohol by reduction of formic acid, see **FORMIC ACID** (p. 533).

**Testing and Estimation.**—Methyl alcohol does not give Lieben's iodoform reaction with iodine and potash (1st *Suppl.* 593; 2nd *Suppl.* 674), and may therefore easily be tested, by means of this reaction, for ethyl alcohol, acetone, and other compounds which yield iodoform when thus treated (Lieben).

The proportion of methyl alcohol in commercial wood-spirit may be estimated as follows:—A dry flask holding 100 c.c., and containing 30 grams of phosphorus di-iodide, is closed with a double-perforated stopper (best of glass) provided with a small tap-burette in which 5 c.c. of the wood-spirit, measured at 16°, are placed. In the other hole a condensing-tube, bent at an obtuse angle, is fitted. The wood-spirit is then added drop by drop, and when all is introduced, the flask is heated for five minutes in boiling water, and then inclined, to distil off the methyl iodide. The receiver consists of a glass tube holding 25 c.c., the lower end being narrowed and calibrated. When the distillation is finished, the condenser is rinsed out with water, the receiver filled with water to the mark, and after the contents have been well shaken, the volume of the iodide is read off. As 5 c.c. of pure methyl alcohol yield under these conditions 7.19 c.c. of iodide, the quantity of the alcohol in the wood-spirit can be found by a simple proportion. If the wood-spirit contains methyl acetate, this compound will also be converted into the iodide; but in the valuation of wood-spirit for the manufacture of aniline-colours, which is the chief object of the process here described, the error arising from this substance may be neglected, because it also forms methylated anilines; moreover its quantity can be easily determined by heating the wood-spirit with standard soda, and finding the quantity used by means of standard acid. Acetone yields, under the above conditions, only a few drops of a distillate which

## METHYL ALCOHOL.

is soluble in water, and the other impurities are converted into resinous bodies (G. Kroll, *Deut. Chem. Ges. Ber.* vi. 1310).

*Mixtures of Methyl Alcohol and Water.*—The specific heats, heat of combination, boiling point, capillarity, expansion by heat, and compressibility of mixtures of methyl alcohol and water in various proportions have been determined by A. Dupré (*Proc. Roy. Soc.* xx. 336).

*Specific Heats.*

Weight per cent. of Methyl Alcohol	Specific Heat referred to Water = 100		Difference
	Found	Calculated	
10	98.682	95.832	+ 2.750
20	95.914	91.065	4.249
30	92.658	87.497	5.161
40	89.210	83.330	5.880
50	84.645	79.162	5.483
60	80.177	74.995	5.182
70	75.500	70.827	4.673
80	69.999	66.660	3.339
90	64.282	62.492	1.790
100	54.325	—	—

*Heat produced by mixing Methyl Alcohol and Water.*

Weight per cent. of Methyl Alcohol	Heat Produced for 5 grams of mixture
10	20.030
20	37.276
30	44.744
40	45.384
50	44.429
60	41.393
70	34.456
80	22.448
90	13.164

*Boiling Points.*

Weight per cent. of Methyl Alcohol	Boiling Point		Difference
	Found	Calculated	
0	99.93	—	—
10	82.57	95.80	- 13.23
20	75.26	91.76	16.50
30	70.68	87.58	16.90
40	68.31	83.40	15.09
50	67.08	79.26	12.18
60	65.75	75.13	9.38
70	64.65	71.00	6.35
80	63.13	66.87	3.74
90	60.96	62.73	1.77
100	58.60	—	—

*Capillary heights of mixtures of Methyl Alcohol and Water in a tube 0.584 mm. diameter, at 13.5°.*

Weight per cent. of Methyl Alcohol	Height referred to Water = 100 mm.	Length of a Water-Column of equal weight	Height calculated	Difference
0	100.00	100.00	—	—
10	68.820	67.818	93.334	- 25.416
20	58.830	57.284	86.667	29.403
30	52.463	50.381	80.001	29.620
40	48.947	46.252	73.335	27.083
50	46.538	43.136	66.668	23.532
60	46.467	42.170	60.002	17.832
70	45.176	40.034	53.336	13.302
80	43.997	37.995	46.669	8.714
90	42.612	35.671	40.003	4.332
100	40.970	33.337	—	—

*Specific Gravities (water = 100,000).*

Weight per cent. of Methyl Alcohol	Specific Gravity at 10°		Difference	Specific Gravity at 20°
	Found	Calculated		
0	99973	—	—	99819
10	98632	97762	+ 870	98384
20	97478	95622	1856	97080
30	96222	93573	2649	95675
40	94729	91611	3118	94054
50	92991	89727	3264	92205
60	91048	87923	3125	90207
70	88933	86188	2745	88035
80	86598	84520	2078	85655
90	84054	82916	1138	83079
100	81371	—	—	80384

*Expansions deduced from the observed Specific Gravities.*

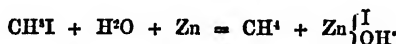
Weight per cent. of Methyl Alcohol	Volume at 10°	Volume at 20°		Difference
		Found	Calculated	
0	100	100.154	—	—
10	100	100.252	100.293	- 0.041
20	100	100.410	100.429	- 0.019
30	100	100.571	100.562	+ 0.009
40	100	100.718	100.689	+ 0.029
50	100	100.853	100.809	+ 0.044
60	100	100.932	100.922	+ 0.010
70	100	101.019	101.028	- 0.009
80	100	101.101	101.124	- 0.023
90	100	101.173	101.212	- 0.039
100	100	101.290	—	—

## Compressibility.

Weight per cent. of Methyl Alcohol	Temperature	Compressibility for one Atmosphere		Difference
		Found	Calculated	
0	16.8	0.00004741	—	—
10	16.5	.00004368	0.00005497	-0.00001129
20	16.0	.00004365	.00006303	.00001938
30	15.4	.00004289	.00007052	.00002763
40	17.4	.00004781	.00007758	.00002977
50	16.5	.00004916	.00008420	.00003504
60	16.4	.00005541	.00009029	.00003488
70	15.7	.00006187	.00009586	.00003410
80	16.3	.00007416	.00010083	.00002667
90	15.2	.00009103	.00010511	.00001408
100	15.0	.00010879	—	—

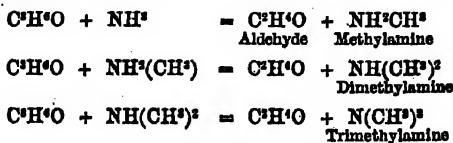
**METHYL ETHERS.** *Chloride*,  $\text{CH}^*\text{Cl}$ .—The best method of preparing this compound is to pass a current of hydrogen chloride into a boiling solution of zinc chloride in twice its weight of wood-spirit, in a flask connected with an inverted condenser and a wash-bottle containing water. The hydrochloric acid is then completely absorbed, and the whole of the methyl alcohol is converted into chloride, while the impurities which accompany it in the wood-spirit are converted into a black tarry mass (Groves, *Chem. Soc. J.* [2], xii. 641).

*Iodide*,  $\text{CH}^*\text{I}$ .—Methyl iodide, in the dry state, is very slowly decomposed by a copper-zinc couple; but if the couple be wet with water, decomposition takes place, even at ordinary temperatures, the products being chiefly methane and zinc iodhydrate:—



With a mixture of methyl alcohol and ethyl alcohol the products are methane and zinc iodethylate,  $\text{ZnI}(\text{OC}^*\text{H}^*)$  (Gladstone & Tribe, *Chem. Soc. J.* [2], xi. 682).

**METHYLAMINE**,  $\text{CH}_3\text{N}$ . *Formation*.—When crude methyl alcohol, after being separated by distillation from pyroligneous acid, is further purified by distillation over lime, the first portion of the distillate has a strong alkaline reaction and an ammoniacal odour, and contains a large quantity of methylamine. If the methyl alcohol be redistilled for a longer time, the quantity of methylamine is increased, and it is accompanied by di- and tri-methylamine. The crude wood-spirit, before these distillations, contains only traces of methylamine, but abundance of ammonia. The ammonia is, therefore, an agent in the production of the methylamine. It does not, however, act directly on the methyl alcohol, for these two bodies may be heated together for several hours without production of methylamine. The reaction takes place between ammonia and acetone, which is always present in crude wood-spirit, as represented by the following equations:—



The aldehyde found in methyl alcohol is derived from the same reaction (C. W. Vincent, *Bull. Soc. Chim.* [2], xix. 14; *Compt. rend.* lxxvii. 898).

According to Berthelot, methyl alcohol and ammonium chloride, heated together to  $320^\circ$ , yield a small quantity of methylamine. Dusart & Berdy (*Compt. rend.* lxxiv. 188), by heating 2 parts ammonium chloride, 3 parts methyl alcohol, and 1 part hydrochloric acid to  $207^\circ$  for 30 hours, obtain oxide and chloride of methyl, together with methylamine hydrochloride amounting to one-third of the ammonium chloride used. From the lower temperature required in this reaction they consider that methyl chloride is essential to it, and that the formation of methylamine in Berthelot's process must have been due to decomposition of the sal-ammoniac into ammonia and hydrochloric acid.

**METHYL-ANILINE.** See ANILINE (p. 73).

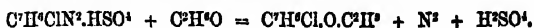
**METHYL-BUTYL CARBINOL**,  $\text{CHOH} \begin{Bmatrix} \text{CH}^3 \\ \text{C}^3\text{H}_7 \end{Bmatrix}$ . See **HEXYL ALCOHOLS** (1st Suppl. 6, 98).

**METHYL-BROMACETOL**,  $\text{CH}^3\text{—CBr}^2\text{—CH}^3$ . Syn. with dibromopropane. See **PROPANES**.

**METHYL-CAPROONE**, or **METHYL-AMYL KETONE**,  $\text{CO} \begin{Bmatrix} \text{CH}^3 \\ \text{C}^5\text{H}_{11} \end{Bmatrix}$ . See **CAPROONE** (p. 251).

**METHYL-CHLORACETOL**,  $\text{CH}^3\text{—CCl}^2\text{—CH}^3$ . Syn. with dichloropropane. See **PROPANES**.

**METHYL-CHLOROPHENETOL**,  $\text{C}^6\text{H}^4\text{Cl.O.C}^3\text{H}^3$ . This compound, the ethylic ether of chlorinated methyl-phenol or chlorocresol, is obtained by heating the sulphate of diazochlorotoluene with absolute alcohol:



*a.* **Methyl-chlorophenetol** prepared from the *a*-diazotoluene salt (obtained by the action of nitrous acid on liquid chlorotoluidine), is an aromatic liquid insoluble in water, easily soluble in alcohol; boils at  $210^\circ\text{--}220^\circ$ ; has a specific gravity of 1.127 at  $19.5^\circ$ .

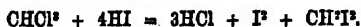
*b.* **Methyl-chlorophenetol**, derived in like manner from solid *β*-chlorotoluidine, has the same odour as the *a*-compound, boils at  $210^\circ\text{--}220^\circ$ , and has a specific gravity of 1.131 at  $18^\circ$ . The *a*-compound is produced in larger proportion than the *β*-compound (Wroblevsky, *Zeitschr. f. Chem.* [2], vi. 164).

**METHYLENE ACETOCHLORIDE**,  $\text{C}^2\text{H}^2\text{ClO}^2$  (L. Henry, *Deut. Chem. Ges. Ber.* vi. 739). When chlorine is passed into cooled methyl acetate until hydrochloric acid is evolved in considerable quantity, and the product is distilled, a portion passes over between  $100^\circ$  and  $120^\circ$ ; and this, when dried and submitted to fractionation, yields methylene acetochloride as a colourless liquid, having a penetrating and suffocating odour, and a burning taste. It has a specific gravity of 1.1953, and a vapour-density of 3.70, is insoluble in water, soluble in alcohol or ether, and boils at  $115^\circ\text{--}116^\circ$ . It is decomposed by water, or alkalis, with formation of hydrochloric acid, acetic acid, and probably formic aldehyde. Sulphuric acid decomposes it, hydrochloric acid being evolved, and a sulpho-acid of methylene [probably  $\text{CH}^2(\text{HSO}^4)^2$ ] being formed. When this acid is distilled with water, it appears to yield formic aldehyde or a polymeric of that substance. When methylene acetochloride is warmed with alcoholic potassium acetate, it yields methylene diacetate; and when it is treated with potassium sulphocyanate, a violent reaction takes place, a substance which has the

composition  $\text{CH}^2 \begin{Bmatrix} \text{CNS} \\ \text{C}^2\text{H}^2\text{O}^2 \end{Bmatrix}$  being probably formed. Ammonia and aniline react on methylene acetochloride, apparently forming methylene bases.

**Methylene formochloride**,  $\text{CH}^2 \begin{Bmatrix} \text{Cl} \\ \text{CHO}^2 \end{Bmatrix}$ , appears to be formed in like manner by the action of chlorine on methyl formate; the product boils at about  $100^\circ$ .

**METHYLENE IODIDE**,  $\text{CH}^2\text{I}^2$ . From experiments by J. Bljuducho (*Zeitschr. f. Chem.* [2], vii. 91) it appears that the greatest yield of this compound is obtained when a mixture of chloroform and hydriodic acid in the proportions required by the following equation is heated to  $130^\circ$  for 24 hours:



**METHYLENE SULPHIDE**. See **THIOFORMIC ALDEHYDE**.

**METHYLENE-PROTOCATECHUIC ACID**. Syn. with **PIPERONYLIC ACID** (q.v.)

**METHYL-GUANIDINE**. See **GUANIDINE** (p. 582).

**METHYL-ISETHIONIC ACID**. See **ISETHIONIC ACID** (p. 705).

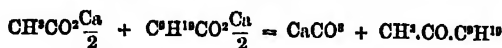
**METHYL KETONES**. **Methyl-propyl Ketone**,  $\text{CH}^3.\text{CO.C}^3\text{H}^7$ , is produced by oxidation of the secondary amyl alcohol obtained from normal pentane (p. 63). It boils at  $102^\circ\text{--}105^\circ$ , unites with alkaline bisulphites, and yields by oxidation, acetic and propionic acids, with a small quantity of carbonic acid (Schorlemmer, *Chem. Soc. J.* [2], x. 1085).

## 808 METHYL KETONES—METHYL-PROPARGYLIC ETHER.

**Methyl-butyl Ketone**,  $\text{CH}_3\text{CO.C}^4\text{H}_9$ , is formed by oxidation of the secondary neryl alcohol obtained from normal hexane (p. 645), and converted by further oxidation into acetic and normal butyric acids (Schorlemmer, *Ann. Ch. Pharm.* clxi, 263).

**Methyl-pentyl Ketone**,  $\text{CH}_3\text{CO.C}^5\text{H}_{11}$ , is formed by oxidation of the secondary alcohol obtained from normal heptane (p. 643). It is a fragrant liquid which boils between  $150^\circ$  and  $152^\circ$ , unites with alkaline bisulphites, and yields by oxidation acetic and normal valeric acids (Schorlemmer, *loc. cit.*)

**Methyl-nonyl Ketone**,  $\text{C}^{11}\text{H}_{22}\text{O} = \text{CH}_3\text{CO.C}^9\text{H}_{19}$ , is produced by distilling a mixture of the calcium salts of acetic and capric acids:



The crude distillate separates by fractional distillation into three portions, the first boiling at  $200^\circ$ , the second at  $210^\circ$ – $215^\circ$ , the third above  $300^\circ$ . The second fraction mixed with alcohol and ammonia, and saturated with sulphurous acid, yields a crystalline ketone-bisulphite which, when purified by crystallisation from alcohol, has the composition  $\text{C}^{11}\text{H}_{22}\text{O} \cdot (\text{NH}_4)\text{HSO}_3 + \text{H}_2\text{O}$ ; and the ketone separated from this salt by sodium carbonate, dried with potash, and rectified, has exactly the composition  $\text{C}^{11}\text{H}_{22}\text{O}$ .

Methyl-nonyl ketone thus prepared is a colourless, strongly refracting oil having an odour slightly resembling that of rue oil, a specific gravity = 0.8295 at  $175^\circ$ , and boiling at  $223^\circ$ – $224^\circ$ . At  $5^\circ$ – $6^\circ$  it solidifies to a crystalline mass, which does not resume the liquid form till heated to  $15^\circ$ – $16^\circ$ . It is insoluble in water, but dissolves easily in alcohol (Gorup-Besanez a. Grimm, *Deut. Chem. Ges. Ber.* iii, 528).

Methyl-nonyl ketone forms the chief constituent of the volatile oil of garden rue (v. 133). Gorup-Besanez a. Grimm, by treating the rectified oil with ammonium bisulphite, obtained a crystalline compound, from which sodium carbonate separated a liquid having a sp. gr. of 0.8281 at  $187^\circ$ , boiling at  $224^\circ$ – $225^\circ$ , and agreeing in melting and solidifying point with the synthetically prepared ketone. Giescke (*Zeitschr. f. Chem.* vi, 429), by subjecting 500 grams of a sample of *Ol. Ruta*, nearly free from hydrocarbons, to fractional distillation, obtained 300 grams of a colourless oil having exactly the composition  $\text{C}^{11}\text{H}_{22}\text{O}$ . It had a violet fluorescence, an odour like that of oranges, a sp. gr. = 0.8268 at  $20.5^\circ$ , boiled at  $225^\circ$ – $226^\circ$ , and solidified at  $6^\circ$  to a mass which melted at  $16^\circ$ . By oxidation with chromic acid mixture, it was converted into pelargonic and acetic acids, agreeing therein with Popoff's law of the oxidation of ketones, according to which the lower alcohol-radicle of the ketone remains with the carbonyl, while the higher radicle is oxidised (p. 711).



Methyl-nonyl ketone, treated with phosphorus pentachloride, is converted into a chloride  $\text{C}^{11}\text{H}_{21}\text{Cl}_2$ , which is resolved by distillation into hydrogen chloride and a chloride  $\text{C}^{11}\text{H}_{21}\text{Cl}$ , boiling at  $221^\circ$ – $223^\circ$ . Both these chlorides, when heated to  $130^\circ$  with alcoholic potash, yield a hydrocarbon of the acetylene series, boiling at  $198^\circ$ – $202^\circ$  (Giescke).

Methyl-nonyl ketone is converted by nascent hydrogen into secondary hendecatyl alcohol,  $\text{CH}_3\text{CHOH.C}^{10}\text{H}_{21}$ . The ketone is placed in a glass cylinder together with a quantity of dilute alcohol not sufficient to dissolve it, and sodium in thin slices is gradually added. On fractionating the crude product, the greater part distills at  $228^\circ$ – $233^\circ$ , leaving a body of very high boiling point, probably belonging to the pinacone group; and by shaking up the portion boiling between  $228^\circ$  and  $233^\circ$  with solution of sodium bisulphite, exhausting the mixture with ether, again treating the residue with sodium bisulphite, and repeating these operations several times, the hendecatyl alcohol is finally obtained free from the ketone.

**Secondary hendecatyl alcohol** is a liquid having nearly the thickness of glycerin, a sp. gr. of 0.826 at  $19^\circ$ , boiling at  $228^\circ$ – $229^\circ$ , insoluble in water. The bromide formed from it by the action of bromine and phosphorus is resolved, on distillation, into hydrogen bromide and hendecatene,  $\text{C}^{11}\text{H}_{22}$ , boiling at  $192^\circ$ – $193^\circ$  (Giescke).

**Methyl-phenyl ketone**,  $\text{CH}_3\text{CO.C}^6\text{H}_5$ . See PHENYL-KETONE.

**METHYL-PHOSPHINES.** See PHOSPHORUS-BASES.

**METHYLPHOSPHOPLATINIC ETHER.** See PHOSPHOPLATINUM COMPOUNDS.

**METHYL-PROPARGYLIC ETHER.** See PROPARGYLIC ETHER.



**METHYL-SALICYLIC ALCOHOL.** An isomeride of ANISIC ALCOHOL,  $C^H^{10}O^2$  (p. 79).

**METHYL-STRYCHNINE.** See STRYCHNINE.

**MICA.** The two following analyses of mica are included amongst the results of the investigation of the mineral constituents of Scotch granites by S. Houghton (*Phil. Mag.* [4], xl. 59): a. From Rubislaw, Aberdeen; large white tables, with angles of  $60^\circ$  and  $120^\circ$ ; angle of the optic axes  $= 72^\circ 30'$ . Contains no lithia. b. Black mica, rarely found in large crystals, but occurring in nearly all granites in the form of small laminae. Contains no fluorine. The specimen analysed is from Aberdeen:—

	SiO <sup>a</sup>	SiF <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	FeO	MnO	CaO	MgO	Na <sup>a</sup> O	K <sup>a</sup> O	H <sup>a</sup> O
a.	44.40	0.16	37.36	2.04	—	0.24	0.78	0.57	0.93	9.87	1.84 = 98.19
b.	36.50	—	16.50	18.49	6.76	1.30	1.11	7.44	0.02	8.77	1.60 = 99.89

In a mica imbedded in selagite, a dark-coloured volcanic rock of Monte Catini, E. Bechi found:—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	MgO	CaO	K <sup>a</sup> O	F	H <sup>a</sup> O
40.8	22.1	21.0	0.5	5.6	5.9	0.8	3.5 = 100.2

Hardness = 2.5. Sp. gr. = 3.15 (*Jahresb. f. Chem.* 1870, 1298).

On the mica of Adamellogranite, see p. 27 of this volume.

**MIGNONETTE.** The root of this plant has a pungent taste, and emits, when cut up, an unmistakable odour of horse-radish. When macerated with hot water and distilled, it yields an oily distillate which is converted into sinapoline by boiling with laryta-water, and into thiosinaminine by treatment with ammonia. These reactions show that the root contains allyl sulphocyanate (A. Vollrath, *Arch. Pharm.* [2], cxlviii. 166).

**MILANITE.** This name is given by E. Tietze (*Jahrbuch geol. Reichsanst.* xx. 588) to a hydrated aluminium silicate from Maidanpek, in Servia, hitherto regarded as agalmatolite. It feels like soap-stone, has a conchoidal fracture, crumbles easily, becomes transiently dark-coloured when heated, and dissolves in hydrochloric acid with separation of silica. It is most nearly related to halloysite. The following analysis by Pateru—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	Fe <sup>a</sup> O <sup>a</sup>	H <sup>a</sup> O
44.96	25.20	trace	29.50 = 99.66

agrees nearly with the formula  $4(Al^aO^a \cdot 2SiO^a) + 27H^aO$ .

**MILARITE.** This mineral was named by Kennigott (*Jahrbuch f. Mineralogie*, 1870, 80) after the Val Milar, near Ruáras, in the canton of Graubünden, Switzerland, where it was supposed to occur; but, according to a notice by Kuschel-Köhler, cited by Frenzel (*ibid.* 1873, 785), it is found, not in the Val Milar, but in the Val Ginf, north-west of Ruáras.

Milarite occurs, together with smoky quartz, orthoclase, apatite, chabasite, titanite, and chlorite, implanted on granite, and forms hexagonal crystals sometimes 10 mm. long, exhibiting the combination  $\infty P2.P$ , frequently also with  $OP$ , more rarely with  $\infty I$ . The terminal dihedral angle of the pyramid was found by direct measurement  $= 144^\circ 48' 5'$ , by indirect measurement  $= 144^\circ 41' 50'$ . Cleavage indistinct, parallel to  $OP$ . The mineral is transparent and nearly colourless, with a faint tinge of green, transparent or translucent, and has a vitreous lustre. Hardness = 5.5 to 6. It swells up and forms a white glass when heated, dissolves but slightly in hydrochloric acid; its powder, both in the natural state and after ignition, has a faint alkaline reaction (Kennigott).

From a quantitative analysis of the mineral, Kennigott inferred that it was a zeolite, consisting of a hydrated silicate of aluminium, calcium, and sodium. Frenzel, however, by a quantitative analysis of pure selected materials, finds its composition to be:—

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	CaO	Na <sup>a</sup> O	H <sup>a</sup> O
71.12	8.45	11.27	7.61	1.65 = 100

The mineral does not sustain any loss of weight at  $100^\circ$ , the water not being given off till the powder is heated to a very high temperature, at which it begins to melt. It is but little attacked by acids.

If the water be regarded as basic, the analytical results may be represented by the formula:



According to this, milarite is not a zeolite, but a mineral related to petalite (Frenzel).

**MILK.** Influence of Food on the production of Milk in the Cow.—G. Kühn and M. Fieischer (*Landw. Versuchstationen*, xii. 197, 361, 405) have made experiments on two

milk-cows, fed daily on a normal diet of 20 lbs. meadow-hay and 0.06 lb. salt, to which were added, in different experiments, known weights of rape-flour, starch, oil, or bruised beans. The results showed that an increase in the production of milk took place after addition of oil or bruised beans, but not after addition of starch or rape-flour. These variations in the feeding affected, however, only the total quantity of milk secreted, its composition remaining nearly the same in all cases. The progress of the lactation was accompanied by a continuous alteration in the composition of the milk of both animals, the total amount of the nitrogenous constituents increasing regularly in proportion to that of the non-nitrogenous constituents, the proportion of milk-sugar and butter steadily decreasing, while the amount of casein increased, and that of albumin diminished, but in smaller proportion. The experiments did not show decidedly whether the formation of butter is due to the carbohydrates or to the albuminous constituents of the food.

These results have been confirmed by a further series of experiments made by Kühn (*Chem. Centr.* 1871, 102; *Chem. Soc. J.* [2], ix. 414) on four cows fed on a diet of moderate amount, not sufficient for the highest yield of milk. The food consisted of hay, barley-straw, and turnips, the albuminous elements of the food being increased at a certain stage of the experiments by the addition of bruised beans.

The general result of these experiments is to show that an increase in the albumin and fatty elements of a moderate diet produces an increase in the milk-yield, which gradually rises (simultaneously with bodily condition) to a certain maximum, corresponding in each case with the maximum increase of the above elements. Sooner or later, however, the natural diminution depending on the period of lactation occurs, and no further increase can be produced by increasing the food. Diminution of the above elements of the food produces a diminution in the milk-yield. The addition of fat increases the ingredients of milk generally, but has no special influence on the amount of fat in the milk. The percentage of sugar in the milk does not appear to be affected by the diet, and the variations in the amount of albumin are too small to be quantitatively determined. No variation in the amount of casein could be traced to the food; indeed, the variations in the percentage of casein and fat appear to be due to irregularities in the action of the gland.

It appears from these results that it is not possible by variations in the food, to produce a 'butter-cow' or a 'cheese-cow.' Differences in this respect are differences of stock and individuals.

For tables of the numerical results of these experiments, see the references above cited.

On the influence of Food on the production of Milk, see further, Fleischer (*Arch. f. pathol. Anatomie*, li. 30; *Jahresb. f. Chem.* 1870, 912); Stohmann (*Zeitschr. f. Biologie*, vi. 204; *Jahresb.* 1870, 911).

Weiske-Proskau (*Ann. d. Landw. Wochenblatt*, Sept. 6, 1871), by experiments on two cows supplied during twelve days with precipitated calcium phosphate in addition to their ordinary food, found that no increase was thereby produced in the percentage of ash, of lime, or of phosphoric acid contained in the milk; neither was there any increase in the absolute quantity of these substances yielded as milk.

According to Stohmann (*Chem. Centr.* 1872, 722) the proportion of phosphoric acid to nitrogen in goat's milk is the same as in the grain of cereals, viz.  $P_2O_5 : N^2$ .

*Reactions of Milk:* (1) *With Litmus.*—The most contradictory statements have been made as to the reaction of normal fresh cows' milk with litmus, numerous observers having found the reaction of milk to be acid, while an equal number describe it as alkaline.

Soxhlet (*J. pr. Chem.* [2], vi. 1; *Chem. Soc. J.* [2], xi. 187) considers that milk possesses what he calls an *amphoteric* or *amphigenic* reaction, i.e. that it has the remarkable property of turning simultaneously red litmus blue and blue litmus red; and this arises from the fact that milk contains both acid and neutral phosphates of the alkali-metals. Heintz maintains that a fluid containing both acid and ordinary alkaline phosphates, simply imparts a violet colour to red and to blue litmus-paper.

A. Vogel (*J. pr. Chem.* [2], viii. 137) has examined this question further, using, instead of litmus-paper, a carefully prepared neutral tincture of litmus, and, as the result of his experiments, states that he has never yet found freshly drawn cows' milk to exhibit a decided alkaline reaction.

If litmus-tincture which has been reddened by milk is left exposed to the air in a watch-glass, it gradually loses the red colour and passes into blue, while, if it be closely corked up, it retains the red colour, though in some cases it seemed to become slightly blue in the course of an hour or two. In either case it acquires, after three or four days, a deep red colour, owing to formation of lactic acid. Hence it follows that in normal fresh cows' milk there is no free lactic acid. Litmus-tincture reddened by milk also becomes blue if shaken up and poured backwards and forwards from one vessel to another, and more especially on heating.

Vogel thinks that the restoration of the blue colour in these cases is due to the escape of the carbonic acid which fresh milk contains. Soxhlet also found that milk, when subjected to the action of the air-pump, gave up carbonic acid and became decidedly alkaline. Other tests for alkalinity in liquids were also applied by Vogel to milk, with negative results.

Out of the milk of 30 cows, which was examined by Bischoff at Schleisheim, only two specimens showed the double reaction with certainty. In the greater number of cases the reaction was either neutral or transiently acid. Some specimens, however, gave, at first, a weak alkaline reaction, quickly passing into acid reaction. This effect was probably due to the absorption of ammonia by the milk, since the experiments were made in the stalls.

(2) *With Boric Acid*.—According to A. Hirschberg (*Chem. Centr.* 1872, 496) the addition of a small quantity of boric acid to milk retards the separation of cream, and preserves the milk from turning sour for several days.

(3) *With Mustard-oil*.—According to Schwalbe (*Deut. Chem. Ges. Ber.* v. 286) the addition of mustard-oil to cows' milk (1 drop to 20 grams) prevents coagulation. The mixture may be kept in summer for weeks in half-filled bottles without coagulating. After 5-7 weeks the casein was found to be converted into albumin, and the liquid was strongly acid.

(4) On the relative quantities of ammonia eliminated from milk by the action of potash and of potassium permanganate, see *ANIMONTA* (p. 61).

*Condensed Milk*.—Trommer (*Dingl. pol. J.* cxviii. 168) prepares condensed milk as follows: 1 part of fresh milk is mixed with 1 part of the cream which rises to the surface when the milk is mixed with sodium bicarbonate in the proportion of  $\frac{1}{2}$  to  $\frac{3}{4}$  oz. of the latter to 10 quarts. The mixture is heated nearly to boiling, then strained, and after addition of pure sugar (in the form of a boiled and clarified solution cooled to 75° C.) in the proportion of 3 to 3½ oz. to a quart, it is evaporated over the water-bath till the residue falls from the stirrer in thick masses. The temperature during the evaporation should not exceed 87-92°. The condensed milk is preserved in tins.

L. Koffer (*Dingl. pol. J.* cxvi. 161) has examined the following kinds of condensed milk: (1.) From the Anglo-Swiss Condensed Milk Company in Cham (Canton Zug); (2.) From the factory in Sassin. (3.) From the Swiss-German Extract Company at Vivis in Switzerland, and Kompten in Bavaria; preserved in glasses. (4.) The same in tins. (5.) From the Emserenth. The various samples contained from 25 to 36 p.c. sugar and 14 to 18 p.c. milk-sugar. These being deducted, the composition of the several sorts is as follows:—

	1	2	3	4	5
Water . . . . .	22.180	18.824	22.421	18.810	20.770
Fat (butter) . . . .	12.260	12.625	12.030	18.650	12.830
Casein and albumin .	28.100	24.240	25.960	24.000	20.600
Ash (salts) . . . .	2.180	2.482	2.673	2.430	2.865

All the samples, when mixed with 4 or 5 times their volume of water, yielded a good sweet milk, and all, when mixed with 5 or 6 vol. water, could be converted into butter, differing from one another only by the greater or lesser facility with which the individual fat-globules ran together.

According to the *British Medical Journal*, Newnham's condensed milk contains 10 p.c. water, 10 casein, 2 ash, 60 fat milk-sugar and cane-sugar. Hence it appears that a pound of the condensed milk contains the constituents of 3 to 4 pounds of fresh milk (*Pharm. J. Trans.* [3], 1, 606).

**Analysis of MILK.** E. H. v. Baumhauer (*Zeitschr. anal. Chem.* ix. 422) discusses the several methods hitherto adopted for the analysis of milk. He rejects as worthless all modes of testing depending on the use of hydrometers, inasmuch as the milk, which is a solution of substances specifically heavier than water, contains in suspension a much lighter body, namely, the cream, and consequently exhibits a mean specific gravity which, after the removal of part of the cream, may be again imparted to the liquid by addition of water. A further objection to the use of hydrometers for the purpose is that the expansion-coefficient of milk is unknown, and moreover uncertain, on account of the varying proportions of the dissolved constituents. To obtain comparable results, it would therefore be necessary to work always at the same temperature. Moreover, the quantity of milk which becomes attached to the unimmersed part of the instrument may give rise to an error equivalent to 5 p.c. of water. In skimmed milk the specific gravity exhibits no constant relation to the sum of the dissolved constituents, since the relative quantities of these are variable. Experiments showed, also, that very little accordance exists between the indications of the cremometer (a graduated glass cylinder in which the volume of cream which rises to the surface on

standing is directly read off) and the amount of fat which can be extracted from the milk by ether. When one cremometer was filled with milk which had not been shaken, a second with milk which had been shaken for a minute, and a third with milk which had been shaken for two minutes, the indications of these instruments varied from 6 to 10 p.c. This diversity is due to the influence of agitation on the mode of separation of the fat-globules.

Heeren (*Dingl. pol. J.* xciii. 396) likewise objects to the use of the cremometer, because only a part of the fat contained in the milk rises as cream to the surface, so that not unfrequently an error of 40 p.c. may occur in the estimation. He further points out that the opacity of milk depends upon the size of the fat-globules, and therefore that all the optical methods depending on comparison of the opacity of a given sample with that of normal milk, must yield different values for the same actual amount of fat present, according as the milk has been skimmed (freed from the larger fat-globules) or not. A difference between the results of the optical and chemical testing indicates previous skimming, inasmuch as perfectly normal milk would exhibit a nearly equal amount of fat by both methods.

The following method of analysis is described by Pribram (*Dingl. polyt. J.* xcvi. 448): 50 grams of the milk are mixed in a tared beaker glass with 15 grams of purified and pulverised common salt, and the mixture, after being stirred with a tared glass rod, is heated to gentle ebullition. After cooling, a quantity of water is added sufficient to raise the liquid contents to 100 grams, care being taken to ensure complete solution and uniform mixture. A large portion of the liquid is then passed through a filter not previously wetted, a portion of the filtrate is exactly weighed out, and the quantity of milk-sugar in it is determined by means of Fehling's solution (10 c.c. = 0.06875 grams of milk-sugar), or better by means of circular polarisation. In another weighed portion of the filtrate, the amount of chlorine—and thence the amount of common salt—is determined by means of a decinormal silver solution. From this the weight of the liquid contents of the beaker, that is to say, the total weight  $x$  of the liquid, is easily determined by means of the proportion—

$$a : b = x : 15$$

where  $a$  is the weight of the filtrate,  $b$  that of the quantity of sodium chloride found therein. The quantity of milk-sugar determined as above is calculated to this quantity of solution, and thence the quantity of milk-sugar in 50 grams is determined.

The remaining contents of the beaker, together with the unused filtrate and any solid portions that may have been collected on the filter, are evaporated to dryness, and the residue is exhausted with ether. This is effected by placing the residue in a glass cylinder connected at one end with a flask containing ether and at the other with an inverted Liebig's condenser, so that the residue is completely exhausted by the condensed ether which runs down upon it. The residue obtained by evaporating the ethereal solution gives the amount of fat.

The residue thus exhausted with ether is dried at  $100^{\circ}$  and weighed. It consists of casein + milk-sugar + sodium chloride, less the portions of the two latter which have passed into the filtrate; and as these have been previously determined, the amount of casein is easily found by subtraction.

The following method is given by Schukoffsky (*Dout. Chem. Ges. Ber.* v. 76) as especially adapted to the analysis of woman's milk: 20 c.c. of ether are added to 20 c.c. of the milk; the mixture is stirred, and to it 30 c.c. of strong alcohol are added. This mixture is allowed to stand for about 24 hours, in which time the milk-sugar separates in crystals on the sides of the vessel. The sugar and casein are filtered off and washed with anhydrous ether and strong alcohol; the filtrate and washings are evaporated on a water-bath till free from alcohol; and the residue is again treated with ether, then allowed to evaporate spontaneously, and finally dried at  $100^{\circ}$  and weighed.

J. A. Wanklyn (*Pharm J. Trans.* [3], i. 606) directs attention to a hitherto unappreciated source of inaccuracy in the ordinary methods of examining milk. He finds that the exact molecular condition of the casein influences the specific gravity of the milk; in other words, that samples of milk of the same strength vary in specific gravity according to the molecular condition of the casein. The following examples are given to show how this may cause a want of correspondence between the specific gravity of milk and the amount of its solid contents. The specimens of milk had been kept in corked bottles for four days.

	Sp. gr. at $60^{\circ}$ F.	Per cent. of solids dried at $212^{\circ}$ F.	Per cent. of ash
Sample A	1.0004	11.34	0.94
" B	0.9960	10.48	0.75
" C	1.0184	8.92	0.66

To be of any value at all, the specific gravity must be taken while the milk is very fresh, for when milk is kept for two or three days, even in a closed vessel, the density falls in a very remarkable manner. Wanklyn therefore proposes, in judging of the strength of milk, to adhere to the method of evaporating to dryness in the water-bath, and weighing the residue, as described in the 1st Suppl. (p. 830).

*Estimation of the Casein in Milk by the Ammonia Process.*—Casein when distilled with alkaline permanganate yields 6.5 p.c. of ammonia. Now normal milk contains 4.0 p.c. casein: consequently 100 parts of milk should give 0.26 p.c. albuminoid ammonia, i.e. ammonia derived immediately from the decomposition of an albuminous body; and this result is confirmed by experiment.

To examine milk by the ammonia process, the following method of procedure may be adopted. Five c.c. of milk are diluted with pure distilled water to half a litre, and 5 c.c. of the dilute milk taken for analysis. 250 c.c. of water perfectly free from ammonia are placed in a retort, together with 50 c.c. of alkaline permanganate solution, and the 5 c.c. of diluted milk added. Distillation is then proceeded with as long as ammonia comes over, the ammonia in the distillate being estimated from time to time by the Nessler test in the usual manner.

The following are some examples of milk analysis by the ammonia process:—

*Milk yielding 12.92 p.c. of Solids, and 8 p.c. of Cream.*

	Quantity of milk taken	NH <sup>3</sup> obtained
I. . .	100 milligrams	0.27 milligram
II. . .	50 "	0.13 "

*Slightly Watered Milk. Solids, 10.20 p.c.*

	Quantity taken	NH <sup>3</sup> obtained
I. . .	100 milligrams	0.22 milligram
II. . .	50 "	0.095 "

*Highly Watered Milk. Solids, 6.18 p.c.*

	Quantity taken	NH <sup>3</sup> obtained
I. . .	50 milligrams	0.075 milligram
II. . .	50 "	{ 0.070 Solids, 8.10 p.c.

In order to translate these results into percentages of casein, all that is required is to multiply the *percentage* of ammonia by 100, and divide the result by 6.5. The figures so obtained represent the percentage of casein in the milk (Wanklyn, *Chem. News*, xxvi. 28).

A. E. Davies (*Chem. News*, xxii. 61) tests milk for adulteration with water by determining the specific gravity of the serum obtained by filtering after the casein and fat have been coagulated. In unadulterated milk this liquid exhibits a tolerably constant density ranging between 1.026 and 1.028.

**MILK-SUGAR.** See SUGAR.

**MILLERITE.** See NICKEL SULPHIDES.

**MILOSCHIN.** An analysis of a specimen of this mineral which had been microscopically examined by Kennigott, and shown to be a mixture of an amorphous substance with numerous crystalline particles, was found by Marco Lecco, of Belgrade, to contain, when dried at 100°, 38.71 p.c. SiO<sub>2</sub>, 43.45 Al<sub>2</sub>O<sub>3</sub>, 0.17 Cr<sub>2</sub>O<sub>3</sub>, and 8.47 water, agreeing approximately with the formula 3SiO<sub>2</sub>.2Al<sub>2</sub>O<sub>3</sub> + 4H<sub>2</sub>O. The analytical numbers differ considerably from those formerly obtained by Kersten (iii. 1024), viz., 27.50 p.c. SiO<sub>2</sub>, 45.01 Al<sub>2</sub>O<sub>3</sub>, 3.61 Cr<sub>2</sub>O<sub>3</sub>, and 23.30 water, the difference doubtless arising from the mixed constitution of the mineral, as shown by the microscopical examination. It is better, therefore, not to regard the mineral as a simple aluminium silicate, represented by the formula 3SiO<sub>2</sub>.2Al<sub>2</sub>O<sub>3</sub> + 4H<sub>2</sub>O, but rather to conclude, from the resemblance of the crystalline particles to many specimens of kaolin when examined by the microscope, that it consists of kaolin (H<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub> + H<sub>2</sub>O.2SiO<sub>2</sub>) imbedded in an amorphous substance having the composition H<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub> + H<sub>2</sub>O.SiO<sub>2</sub>. This view represents the mineral as allied to the species called carolathin (Kennigott, *Jahrbuch. f. Mineralogie*, 1872, 951).

**MILLET.** Under the general name of millet are included various species of *Panicum*, *Setaria*, and *Sorghum*; only those growing in temperate climates have been examined by the chemist.

The seeds of *Panicum miliaceum* (Fr. millet, Ger. Hirse) serve as human food.

*Setaria italica* (Fr. Millet des oiseaux, Ger. Mohar) is used in the green state as fodder for horses in Hungary; the seeds form the ordinary bird-millet. *Sorghum vulgare* (Fr. millet grand, Ger. Mohrhirse), the Durra of Egypt and India, also known as Guinea-corn, has the largest grain of any of the millets, and in hot countries is extensively grown as human food. *Sorghum saccharatum* (Fr. millet noir, Ger. Zucker-mohrhirse) is also largely grown in China and in other warm countries; the seed is employed as human food, while from the ripe stalks sugar may be extracted.

In the following table is given the mean of the analyses made. The composition given for Sorghum is the average adopted by Wolff.

	Number of analyses	Water	Albumi- noids	Fat	Extract- ive matter	Fibre	Ash
<i>Composition of Millet-grain.</i>							
<i>Panicum miliaceum</i> , with husk	1	13.15	10.91	3.67	56.89	13.06	2.32
<i>Panicum miliaceum</i> , without husk	3	13.03	15.39	5.05	62.08	2.71	1
<i>Composition of Millet-hay.</i>							
<i>Setaria italica</i>	4	12.75	10.28	2.34	38.61	30.13	5.89
<i>Composition of Green Sorghum.</i>							
<i>Sorghum vulgare</i>	—	77.3	2.9	11.9		6.7	1.1
<i>Sorghum saccharatum</i>	—	74.0	2.5	1.4	13.0	7.3	.9

The grain of *P. miliaceum*, when deprived of the husk, contains, according to the complete analysis of Pillitz: Water, 12.9; starch, 60.22; dextrin, 1.12; sugar, .45; cellulose, 3.73; soluble albuminoid, 1.18; insoluble albuminoid, 14.11; soluble ash, 1.03; insoluble ash, .56. Guinea-corn, from the West Indies, contains, according to analyses by Dr. Sheir and Johnston, 7.43 p.c. of albuminoids. A specimen of Durra gave Johnston 11.19 p.c. of albuminoids; it contained legumin.

The sap of *S. saccharatum*, according to C. T. Jackson (*Jahresb. Agri. Chem.* 1858, 79), contains glucose till ripening commences, when cane-sugar is developed. J. Moser (*Jahresb. Agri. Chem.* 1866, 315) found in the sap pressed from the stalks at the end of October, 12.45 p.c. of cane-sugar, and 2.32 p.c. of fruit-sugar. Voelcker (*Jour. Roy. Agri. Soc.* xx. 378) found no sugar in sorghum grown in England at the middle of August; a month afterwards it amounted to 5.85 p.c. of the plant.

Metzdorf (*Jahresb. Agri. Chem.* 1860, 136) made a complete examination of German millet (*Setaria italica*) in five stages of growth; the results are an excellent illustration of the change in composition which a plant undergoes as it develops.

*Percentage composition of Setaria italica, whole plant, dried at 100°.*

	July 11, height 3-4 inches	July 26, height 8-10 inches	August 10, height 18-16 inches	August 24, in bloom, 15-24 inches	Septem- ber 7
Albuminoids	25.72	25.01	19.44	17.01	15.97
Extractive matter and fat	37.29	37.75	41.46	43.33	43.76
Fibre	23.93	25.67	31.30	32.96	31.22
Ash	13.06	11.57	7.31	6.65	6.66
Water in fresh state	80.95	78.65	69.91	66.36	64.99

Percentage Composition of the Ash.

	July 11, height 8-9 inches	July 20, height 8-10 inches	August 10, height 15-16 inches	August 24, in bloom, 18-24 inches	Septem- ber 7
Potash . . . . .	57.90	54.59	38.75	36.01	27.49
Soda . . . . .	.81	none	none	none	none
Lime . . . . .	4.84	5.56	9.67	11.91	7.42
Magnesia . . . . .	6.50	6.22	9.80	6.14	11.83
Oxide of iron . . . . .	.73	1.20	.73	.70	.64
Phosphoric acid . . . . .	4.88	4.76	5.40	5.47	5.84
Sulphuric acid . . . . .	3.58	3.22	3.65	3.54	3.43
Chlorine . . . . .	7.61	8.94	7.44	5.43	4.34
Silica . . . . .	15.06	17.52	26.23	32.03	39.99

In the above table the increase of fibre, and the diminution of albuminoids and ash as the plant matures, are plainly seen. In the composition of the ash the diminution of potash and chlorine, and the increase in silica, lime, and magnesia, are equally evident. The carbonic acid of the ash has evidently been deducted, and the ash re-calculated to 100 parts.

The following are the mean ash analyses of millet-grain :—

	Number of analyses	Ash in dry	K <sup>2</sup> O	Na <sup>2</sup> O	MgO	CaO	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	SiO <sup>2</sup>
<i>Panicum miliaceum</i> , with husk . . . . .	2	4.49	11.9	1.0	8.4	1.0	23.4	.2	52.3
<i>Panicum miliaceum</i> , without husk . . . . .	2	1.38	19.3	4.0	22.2	none	50.5	2.1	none
<i>Sorghum vulgare</i> . . . . .	1	1.86	20.3	3.3	14.8	1.3	50.9	—	7.5

R. W.

**MOLECULE.** According to Avogadro's law, which, as already shown (p. 546), is a necessary consequence of the physical constitution of gases, all perfect gases at equal pressure and temperature contain equal numbers of molecules in equal volumes. Hence it follows that the weights of the individual molecules of any two gases are proportional to the weights of equal volumes of these gases at equal pressure and temperature—that is to say, to their specific gravities.

If now we express the specific gravities of gases on the hydrogen scale, in other words, if we assume as the unit of volume, that volume of hydrogen which weighs the unit of weight (say 1 gram), the specific gravities, or weights of equal volumes, of some of the more important gaseous elements and compounds will be represented by the following numbers—

	Weight of 1 volume	Weight of 2 volumes
Hydrogen . . . . .	1	2
Chlorine . . . . .	35.5	71
Oxygen . . . . .	16	32
Nitrogen . . . . .	14	28
Hydrochloric acid . . . . .	10.25	36.5
Water-vapour . . . . .	9	18
Ammonia . . . . .	8.5	17
Marsh-gas . . . . .	8	16

Now hydrochloric acid gas is formed by the combination of equal volumes of hydrogen and chlorine united without condensation, or 2 volumes of hydrochloric acid gas are made up of 1 vol. hydrogen and 1 vol. chlorine, the weights of which are as 1 to 35.5. Hence it is assumed that a molecule of hydrochloric acid contains 1 atom of hydrogen and 1 atom of chlorine; and, taking the weight of the atom of hydrogen as 1, the weight of the atom of chlorine will be 35.5, and that of the molecule of hydrochloric acid 36.5.

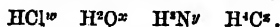
Secondly, the specific gravity of water-vapour on the hydrogen scale being 9, the weights of equal volumes of hydrochloric acid gas and water-vapour are as the

numbers 36.5 and 18. This last number represents therefore the molecular weight of water-vapour; and since 18 parts of water contain 2 parts hydrogen and 16 of oxygen, it follows that the molecule of water contains 2 atoms of hydrogen.

In like manner it is found that the molecular weight of ammonia gas is 17, and that it contains 3 parts by weight, or 3 atoms, of hydrogen united with 14 parts by weight of nitrogen; also that the molecule of marsh-gas weighs 16, and contains 4 parts by weight, or 4 atoms, of hydrogen.

These conclusions respecting the numbers of hydrogen-atoms contained respectively in the molecules of hydrochloric acid, water, ammonia, and marsh-gas, are confirmed by the well-known differences in the behaviour of these compounds with regard to their power of taking up other elements in exchange for hydrogen, the hydrogen in marsh-gas being replaceable by *fourths*, that of ammonia by *thirds*, that of water by *halves*, while that of hydrochloric acid can be replaced only *as a whole*, the quantity of hydrogen in the molecule of hydrochloric acid being indivisible, or, in other words, an atom.

The structure of the molecules of the four compounds may therefore, so far as the preceding considerations are concerned, be represented by the formulæ—



The reasons for regarding the indices  $w$ ,  $x$ ,  $y$ ,  $z$ , as all equal to unity, or for representing the compounds in question by the formulæ—



are fully developed in the article **ATOMIC WEIGHTS** (i. 456-463) and need not be here repeated.

The weights of equal volumes of hydrochloric acid, hydrogen, chlorine, oxygen, and nitrogen being as the numbers

36.5    2    71    32    28,

and the first of these numbers representing the weight of a molecule of hydrochloric acid, it follows that the molecules of hydrogen, chlorine, oxygen, and nitrogen weigh respectively 2, 71, 32, and 28, inasmuch as any given volume of either of these gases contains the same number of molecules as an equal volume of hydrochloric acid; and as these numbers are the doubles of the respective atomic weights, it follows that *a molecule of each of these elementary gases is made up of two atoms*, so that these gases in the free state may be represented by the formulæ—



The same considerations are of course applicable to the vapours of bromine, iodine, sulphur, and selenium.

With regard to these gases then the law holds good that: *Equal volumes of Elementary Gases contain equal numbers of Atoms*. The exceptions presented to this law by the vapours of phosphorus, arsenic, mercury, and cadmium have been discussed in the article relating to the Combining Volumes of Gases (ii. 810).

It is unnecessary to pursue the subject further in this place, as the determination of atomic weights and the volume-relations of gases have already been fully considered from different points of view in previous articles (**ATOMIC WEIGHTS**, i. 455-466, and **GASES, COMBINATION OF**, BY VOLUME, ii. 809-812).

The object of the preceding considerations is to show how the determination of the atomic and molecular weights of gaseous elements and compounds may be established on the basis of Avogadro's law.

See further Gmelin-Kraut's *Handbuch der Chemie*, Erster Band, Erste Abtheilung, pp. 29-34; also Cannizzaro, *Considerations on some Points in the Theoretic Teaching of Chemistry* (Chem. Soc. J. [2], x. 941-967).

**MOLYBDENUM.** *Atomic Weight.*—Lothar Meyer (*Ann. Ch. Pharm.* clxix. 360) from the analysis of the chlorides, and the conversion of the trichloride into tri sulphate (making use of the atomic weights of silver, chlorine, and sulphur, determined by Stas), estimates the atomic weight of molybdenum at 95.8.

**Chlorides.** These compounds have recently been examined by Liechti & Kamps (*Ann. Ch. Pharm.* clxix. 344), who have confirmed the result obtained by Debray (*1st Suppl.* 831) that the highest chloride, obtained by heating metallic molybdenum in chlorine gas, is a pentachloride,  $\text{MoCl}_5$ . To prepare this compound, metallic molybdenum is heated in a stream of dry hydrogen chloride as long as any woolly sublimate is formed; this sublimate is driven out of the tube by heat; the tube filled with the hydrochloric acid gas is left to cool; dry chlorine gas is then passed through it for an hour to expel all remaining atmospheric air from the apparatus; and the metal



is heated till it begins to glow and brown-red vapours begin to appear. By careful heating the whole of the metal may be converted in a short time into the black pentachloride.

The pentachloride heated to about  $250^{\circ}$  in a stream of hydrogen is reduced to the red, difficultly volatile trichloride,  $\text{MoCl}_3$  or  $\text{Mo}^{\text{III}}\text{Cl}_3$ ; and this compound, heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved, according to the equation  $\text{Mo}^{\text{V}}\text{Cl}_5 = \text{MoCl}_3 + \text{MoCl}_2$ , into the yellow dichloride which remains in the tube, and the brown tetrachloride which sublimes or is carried forward by the stream of gas.

Of these four chlorides the pentachloride is the only one which crystallises distinctly, and melts and volatilises without decomposition. The pure pentachloride is black; the green shimmer ascribed to it by Dobray indicates admixture of oxychloride. Its vapour has a dark brown-red colour. The sulphur-yellow dichloride and the red trichloride, which is deceptively like amorphous phosphorus, have been obtained only in the amorphous state; the tetrachloride is an indistinctly crystalline brown sublimate. In an atmosphere of carbon dioxide the dichloride bears a bright red heat without melting or volatilising; the trichloride under the same circumstances is resolved into di- and tetrachloride, which when again heated splits up into pentachloride which sublimes, and trichloride which remains behind.

The di- and trichloride are quite permanent in the air at ordinary temperatures, and insoluble in water; the tetra- and pentachloride on the other hand are extremely susceptible of the action of oxygen, and more particularly of moisture, so that their manipulation is attended with great difficulty.

The dichloride is insoluble in *nitric acid*, which, however, dissolves all the other chlorides. The dichloride dissolves easily in hot *hydrochloric acid*, with aid of heat, and crystallises therefrom on cooling, in long, shining, yellow needles, having the composition  $\text{Mo}^{\text{II}}\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ . The crystals when heated to  $100^{\circ}$  give off two-thirds of their water without disintegrating, losing, however, little hydrochloric acid at the same time. At a somewhat higher temperature the loss of hydrochloric acid is more considerable, the greater part of the salt being, however, converted into the anhydrous dichloride, which retains the form of the crystals, and may be recrystallised from water.

**Trioxide,  $\text{MoO}_3$ .** *Recovery from the residues of Phosphoric Acid determinations.*—

F. Muck (*Zeitschr. anal. Chem.* viii. 377) treats the filtrate from phosphoric acid precipitations with solution of sodium phosphato (1 part  $\text{P}_2\text{O}_5$  to 30 parts  $\text{MoO}_3$  of the quantity of the latter is previously known). The yellow precipitate of ammonium phosphomolybdate is collected on a filter, washed with water, dried and weighed, and to 100 parts of it are added 360 parts of ammonium, 1,350 nitric acid, and 2 to 3 parts pure magnesia, the magnesia being dissolved in the requisite quantity of nitric acid, the yellow precipitate in the smallest possible quantity of ammonia, the two solutions united, and the liquid after standing for some time filtered from the ammonio-magnesian phosphate. This latter precipitate is washed with the remainder of the weighed quantity of ammonia, the filtrate is poured into the bulk of the nitric acid, and the yellow precipitate which separates after a while is removed by filtration. The filtrate, which contains about 5 p.c. molybdenum trioxide, is now again ready for use.

Fresenius (*ibid.* x. 204) evaporates the filtrate from phosphoric acid precipitations to dryness, and ignites the residue till the ammonium nitrate has for the most part been destroyed; the residue is then digested with ammonia, which dissolves out the molybdic acid. The filtered solution is treated with sufficient magnesia mixture to precipitate any phosphoric acid that may be present. The precipitate, if any, is allowed to subside well before filtering, and to the filtrate is added just sufficient nitric acid to render the liquid slightly acid. Molybdic acid is thus precipitated, and may be obtained pure by syphoning off the supernatant liquid, and washing with a little water. The filtrate contains but little molybdic acid, and can be worked up again with fresh residues.

Fresenius prefers this method to that of Muck above described. Muck on the other hand (*ibid.* x. 307) objects to Fresenius's method that it involves the evaporation of large quantities of liquid, the addition of ammonium salts, and the treatment of the residue after evaporation with ammonia, which last operation is often very troublesome, in consequence of the presence of iron and calcium salts.

**Estimation.**—Chatard (*Deut. Chem. Ges. Ber.* iv. 280) adds to the boiling solution of a molybdate a slight excess of lead acetate, and boils the resulting precipitate for about two minutes, whereupon it becomes granular and quickly settles down. It is then washed, first with pure water, afterwards with a very dilute solution of ammonium nitrate, dried at  $100^{\circ}$ , separated from the filter, and ignited in a porcelain crucible.

**Reaction with Phosphorus Trichloride.** See PHOSPHORUS CHLORIDES.

**MONAZITE.** *Native Cerous Phosphate.*—G. vom Rath (*Jahrbuch f. Mineralogie*, 1871, 172) observed in a cavity of a sunadine bomb from Lake Laach a crystal of orthite, on which lay another crystal, 1 mm. in length, olive-green in colour, and with a brilliant lustre; the latter he believes to be monazite, a mineral hitherto unknown not only at Laach, but in any volcanic rocks whatever; from its minute size he was unable to analyse it, but its immediate association with the orthite renders it highly probable that it also is a cerium compound. The crystal is tabular and exhibits the form,  $+P, \pm P\infty, (P\infty), \infty P, (\infty P\infty)$  and  $\infty P\infty$ . Ratio of clinodiagonal : orthodiagonal : principal axis = 0.965886 : 1 : 0.92169; angle of inclined axes  $103^{\circ} 28'$ . The directions of cleavage of the Laach crystal also accord with those of monazite. A strong lustre arising from internal fissures is seen along the edges of the positive and negative hemidomes, and indicates a distinct direction of cleavage parallel to the base which does not form a face of the crystal. There is a second cleavage parallel to the orthopinacoid. Monazite has hitherto been found only in the old plutonic rocks or in alluvium derived from them; its mode of occurrence in Lake Laach therefore is peculiar. It furnishes a second instance of the occurrence of a cerium mineral in volcanic masses, vom Rath having previously found orthite (cerium silicate) at Lake Laach and on Monte Somma.

**MONTEBRASITE.** See PHOSPHATES OF ALUMINIUM.

**MONZONITE.** This mineral, from the Monte Monzoni in the Fassa Valley, near the small lake of La Selle, is compact and occurs in fragments. Hardness = 6; sp. gr. = 3. Fracture, splintery to imperfectly conchoidal. Colour, light green, like that of many green hornstones. Slightly translucent on the edges. Melts easily before the blowpipe to a shining greyish-green glass. Gives off a little water when heated in a tube. Insoluble in hydrochloric and sulphuric acid, but dissolves in strong aqueous phosphoric acid. Analysis gave—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	FeO	CaO	MgO	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O
62.60	17.10	0.00	0.65	2.10	6.60	1.90	1.50 = 100.45

leading to the formula  $12(R'O.SiO^2) + 4Al^2O^3.9SiO^2$ . The mineral, when examined in a thin slice under the microscope, shows no signs of mixed constitution, and may therefore be regarded as a distinct species (F. v. Kobell, *Jahrbuch f. Mineralogie*, 1871, 640).

**MORPHINE.**  $C^8H^8N^2O^4$ .—*Detection.* According to Flückiger (*Arch. Pharm.* [3], i. 117), morphine may be detected in a solution containing 1 part in 100 by the addition of chlorine-water and ammonia. A red colour is thereby produced, which soon changes to brown. The iodic acid reaction, however (iii. 1052), by which a brown colour is produced and the odour of iodine developed, is capable of detecting about 1 part in 10,000.

*Detection in Quinine.*—Morphine may be detected in quinine by adding a little of the salt to a solution of potassium ferrocyanide mixed with ferric chloride and a small quantity of hydrochloric acid. If morphine (or any other deoxidising substance) is present, the solution speedily becomes blue (H. Hager, *Chem. Centr.* 1872, 727).

*Separation of Morphine and Strychnine.*—Otto, in his 'Anleitung zur Ermittlung der Gifte,' states that these two alkaloids may be separated by agitating the solution, previously rendered alkaline, with ether, the strychnine then dissolving in the ether, while the morphine remains in the aqueous liquid. Neubauer, however, finds that the separation is not complete, the earlier ethereal extracts containing a mixture of strychnine and morphine, while the later ones yield crystallisations in which only morphine can be detected. From the residues exhausted by ether, an additional quantity of morphine can always be extracted by amyl alcohol (*Zeitschr. anal. Chem.* ix. 134).

For the detection of morphine Neubauer recommends the test proposed by Fröhde (*Zeitschr. anal. Chem.* v. 214), which consists in adding to the suspected liquid a recently prepared solution of molybdic acid in strong sulphuric acid, whereupon the liquid assumes a violet colour, changing to blue and dirty-green.

*Estimation of Morphine in Opium.*—Methods of estimation founded on the liberation of iodine from iodic acid by morphine are given by W. Stein (*Arch. Pharm.* [2], cxviii. 156; *Chem. Soc. J.* [2], x. 180), and by J. T. Miller (*Pharm. J. Trans.* [2], ii. 466, *Chem. Soc. J.* [2], x. 181).

A modification of Guillemond's method of estimation (iii. 1053) is described by Revell (*Monit. Scient.* xiii. 312; *Jahresb. f. Chem.* 1871, 824).

*Morphine Salts.* *Acetate.*—J. M. Marsch (*Pharm. J. Trans.* [2], i. 304), observes

that aqueous solutions of officinal alkaloid salts, especially of morphine acetate, are apt to deposit quantities of flocculent substance. In a solution of morphine acetate in which this had taken place, nearly all the acetic acid had disappeared, and the morphine had separated in crystals.

**Hydrocyanide.**—A solution of pure ammonium cyanide added to a neutral morphine solution (even diluted to  $\frac{1}{100}$ ) throws down a crystalline precipitate of morphine hydrocyanide, very slightly soluble in water (Marsch, *ibid.* 1005).

#### Derivatives and Polymerides of Morphine.

**Nitrosyl-derivatives.** When morphine suspended in water is subjected to a very rapid stream of nitrous acid vapour (obtained from nitric acid and arsenious acid) a yellow to reddish-yellow crystalline powder (A) is obtained, having the composition  $C^{17}H^{19}(NO)^2N^2O^4 + 2H^2O$ . It produces a black colour with ferric chloride, and gives off its water at  $125^\circ$ . By gradually dissolving this substance in considerable quantities of alcohol and distilling off the alcohol, a compound,  $C^{17}H^{19}(NO)^2N^2O^4 + 4H^2O$ , (B) is produced, which, when boiled with water, gives off an inodorous gas, and yields a filtrate which deposits a finely divided precipitate (C). The residue (D) left after repeated boiling has, after solution in large quantities of alcohol and distillation of the alcohol, the composition  $C^{17}H^{19}N^2O^4$ . When the body A is treated in the cold with a mixture of  $\frac{1}{3}$  strong sulphuric acid and  $\frac{2}{3}$  part water, a violent evolution of vapours takes place, which turns red in contact with the air, and a substance (E) is formed, insoluble in the resulting liquid. The same substance is formed, with evolution of an inodorous gas, by similar treatment of D. This substance does not exhibit any particular reaction with ferric chloride. Strong sulphuric acid colours it yellow with a tinge of red. Its analysis gave numbers which may be represented by the formula  $C^{17}H^{19}N^2O^4 \cdot 2H^2O \cdot H^2SO^4$ . The base of this salt is precipitated by ammonia in a state of very fine division; it gives a black colour with ferric chloride, but has not been further investigated. The body A has the composition of morphine nitrite, but does not appear to be identical therewith; neither does the body D appear to be identical with Schützenberger's oxymorphine (1st Suppl. 849).—(E. L. Mayer, *Deut. Chem. Ges. Ber.* iv. 121).

**Chlorinated Derivative produced by the action of Hypochlorous acid.** When a solution of morphine in excess of hydrochloric acid is treated with chloride of lime, greenish flocks are obtained, which, after solution in alcohol, precipitation with water, solution in ether, and distillation of the latter (whereby the flocks are converted into an oil which solidifies to a crystalline mass) have the composition  $C^{17}H^{19}Cl^2N^2O^4$  (Mayer, *loc. cit.*)

**Acetyl Derivatives** (Wright, *Chem. Soc. J.* [2], xii. 1033). Three of these bodies have been obtained, viz.—

Monoacetyl-morphine	$C^{17}H^{17}(C^2H^3O)N^2O^4$ ,
Diacetyl-morphine	$C^{17}H^{15}(C^2H^3O)^2N^2O^4$ ,
Tetraacetyl-morphine	$C^{17}H^{13}(C^2H^3O)^4N^2O^4$ .

They are produced by the action of acetic acid and acetic anhydride on morphine. Tetraacetyl-morphine is formed by treating morphine with acetic anhydride in excess. Diacetyl-morphine is known in two modifications, one of which ( $\alpha$ ) is produced by heating morphine with glacial acetic acid, the other ( $\beta$ ), by the action of acetic anhydride, in quantity less than sufficient to form tetraacetyl-morphine. Monoacetyl-morphine is produced by heating morphine to  $100^\circ$  for an hour, with a quantity of acetic anhydride considerably less than that which is required to produce  $\beta$  diacetyl-morphine.

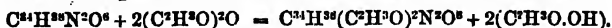
**Monoacetyl-morphine** precipitated from the solution of its acetate, which is the direct product of the reaction above mentioned, by sodium carbonate, exhibits properties very much like those of  $\beta$  diacetyl-morphine (*infra*). It is soluble in ether, a property which shows that it is not a mere mixture of morphine and diacetyl-morphine, since morphine itself is nearly insoluble in ether. Its hydrochloride,  $C^{17}H^{17}(C^2H^3O)N^2O^4 \cdot 2HCl$ , obtained by treating the base with a quantity of hydrochloric acid less than sufficient to dissolve the whole, dries up to a varnish over sulphuric acid, whereas a mixture of the hydrochlorides of morphine and diacetyl-morphine in equal quantities dissolved in a little water allows almost the whole of the former to crystallise out, and dries up to a crystalline mass wetted by a syrup which finally dries up to a glaze over the crystals. The platinochloride prepared with the neutral liquid obtained by shaking up the ethereal solution of the base with hydrochloric acid, has the composition  $C^{17}H^{17}(C^2H^3O)N^2O^4 \cdot 2HCl \cdot PtCl^4$ .

The existence of this monoacetyl derivative shows that the ordinary formula of morphine,  $C^{17}H^{19}NO^4$ , must be doubled.

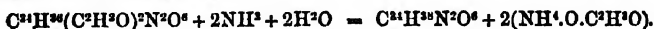
*a. Diacetyl-morphine* is obtained, together with the  $\beta$  modification, by boiling morphine for several hours with twice its weight of glacial acetic acid in a vessel with inverted condenser. On dissolving the product in water, adding ammonia, and shaking up with ether, an ethereal solution is obtained which when shaken with hydrochloric acid yields a copious crystalline hydrochloride; and from this salt the base may be separated by ammonia as a flocculent non-crystalline precipitate, easily soluble in ammonia, sodium carbonate, caustic potash, ether, alcohol, and benzene; from the last three solutions it separates by spontaneous evaporation as a gummy mass. It has also been obtained by a process the description of which is not yet published, in crystals containing  $C^{11}H^{10}(C^2H^3O)^2N^2O^6 + 2H^2O$ . The *hydrochloride*,  $C^{11}H^{10}(C^2H^3O)^2N^2O^6 \cdot 2HCl + 6H^2O$ , is but sparingly soluble in cold water, but may be recrystallised without change from hot water. The *platinochloride*,  $C^{11}H^{10}(C^2H^3O)^2N^2O^6 \cdot 2HCl \cdot PtCl_4$ , is amorphous.

When pure neither the free base nor its salts give any coloration with ferric chloride; this property distinguishes the  $\alpha$  from the  $\beta$  modification, which gives a blue colour.

*B. Diacetyl-morphine* is the chief product obtained by heating morphine to  $100^\circ$  for an hour with the quantity of acetic anhydride required by the equation

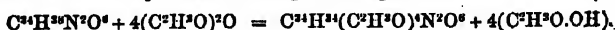


The free base separated from the acetate by sodium carbonate is readily soluble in ether, ammonia, sodium carbonate, and caustic potash, and is precipitated from its salts in amorphous flakes by alkalis. It is much less stable than  $\alpha$ -diacetyl-morphine, ordinary morphine soon crystallising out from its ammoniacal solution while ammonium acetate remains dissolved—



The *hydrochloride*,  $C^{11}H^{10}(C^2H^3O)^2N^2O^6 \cdot 2HCl$ , obtained by treating the base with a quantity of hydrochloric acid not sufficient to dissolve the whole, dries up over sulphuric acid to a gummy mass, which if perfectly dry may be heated to  $100^\circ$  without decomposition, but is decomposed by heating if moist, giving off acetic acid. By boiling with water, or by contact with excess of hydrochloric acid, it is decomposed like the free base, morphine hydrochloride crystallising out, and acetic acid being set free. It is extremely hygroscopic and strikes a blue colour with ferric chloride.

*Tetracetyl-morphine*,  $C^{11}H^{10}(C^2H^3O)^4N^2O^6$ , is produced by treating morphine with excess of acetic anhydride, according to the equation—

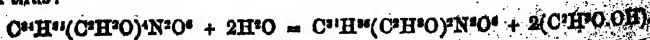


The same result is brought about whether the materials are allowed to remain in contact at the ordinary temperature for several days, or heated to  $100^\circ$  or to  $140^\circ$  for some hours; on adding sodium carbonate to the product dissolved in water, a precipitate is obtained, flocculent at first, but soon becoming crystalline; this dissolves readily in ether and is obtained in fine anhydrous crystals by evaporation; it can also be recrystallised without change from hot alcohol or benzene, and from chloroform; long-continued boiling with alcohol partially decomposes it, whilst boiling with water quickly alters it.

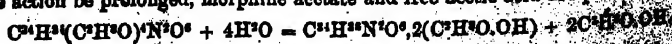
Tetracetyl-morphine gives no colour-reaction with ferric chloride; like morphine, it is but very sparingly soluble in ammonia and sodium carbonate, but dissolves readily in caustic potash. When *exactly* neutralised with dilute hydrochloric acid, it yields a solution which on standing over sulphuric acid deposits crystals of the *hydrochloride*,  $C^{11}H^{10}N^2O^6 \cdot 2HCl$ ; these are extremely soluble in water, so that they form only just before the whole mass has evaporated to dryness; if any excess of hydrochloric acid be present, partial decomposition takes place during the evaporation, acetic acid being evolved.

The *platinochloride*,  $C^{11}H^{10}N^2O^6 \cdot 2HCl \cdot PtCl_4$ , is amorphous.

Tetracetyl-morphine when boiled with water gradually dissolves; and if the process be interrupted just as the last portions are on the point of solution (at the end of an hour or two) the liquid consists almost wholly of acetate of  $\alpha$ -diacetyl-morphine, formed thus:—



If the action be prolonged, morphine acetate and free acetic acid are produced

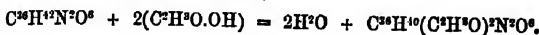


The syrupy mother-liquors from which tetracetyl-morphine has crystallised, slowly

contain more or less  $\alpha$ -diacetyl-morphine, probably formed by the action of the trace of water taken up by the ether used in the preparation of the tetracetyl-morphine.

*Appendix to the Acetyl-derivatives of Morphine.*

**Diacetyl-codeine**,  $C^{10}H^{14}N^2O^4 = C^{10}H^{14}(C^2H^3O)^2N^2O^2$ . This base is produced by boiling codeine dried at  $140^\circ$  with twice its weight of glacial acetic acid for eight hours in a vessel with inverted condenser:



On evaporating the resulting liquid to dryness on the water-bath, dissolving the residue in water, and adding sodium carbonate, a white precipitate is thrown down, flocculent at first, but soon becoming crystalline on standing; by rapid filtration this is separated from unaltered codeine, which is not immediately precipitated in this manner, save in very concentrated solutions. By dissolving the precipitate in dilute hydrochloric acid, and repeating the precipitation by sodium carbonate three or four times, a product is obtained quite free from codeine; the last precipitate is dissolved in ether or hot dilute alcohol, from either of which solvents the diacetyl-codeine crystallises in bold, well-defined anhydrous crystals; it can also be recrystallised from benzene, chloroform, and boiling water without change, being readily soluble in all these solvents except water, in which it is only sparingly soluble even when boiling.

Diacetyl-codeine salts give no coloration with ferric chloride; the precipitated base is but slightly soluble in ammonia or in sodium carbonate, but dissolves more readily in caustic potash.

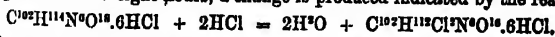
The *hydrochloride*,  $C^{10}H^{16}N^2O^5.2HCl + 4H^2O$ , crystallises well, and dissolves in water more freely than the hydrochloride of codeine. The *platinochloride*,  $C^{10}H^{16}N^2O^5.2HCl.PtCl_4$ , is a yellow non-crystalline precipitate.

No other acetyl-derivatives of codeine have yet been obtained (Wright).

*Polymerides of Morphine and their Derivatives.*

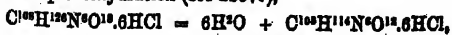
1. **Polymerisation by the action of Sulphuric acid.** The investigations of Arppe and of Laurent a. Gorhardt led to the conclusion that the final product of the action of dilute sulphuric acid upon morphine was a kind of amide called *sulphomorphide*, having the composition of morphine sulphate minus water (iii. 1065). Matthiessen a. Wright, however (*Proc. Roy. Soc.* xvii. 455), in repeating Arppe's experiments, obtained a small quantity of a base exhibiting the quantitative reactions of apomorphine; and Wright (*Chem. Soc. J.* [2], xi. 220) has shown that the main result of the action of dilute sulphuric acid on morphine, first at  $100^\circ$  and afterwards at  $140^\circ$ , is *polymerisation without dehydration*, the products successively formed being trimorphine,  $C^{102}H^{114}N^6O^{18}$ , homologous with tricodeine, and tetramorphine,  $C^{122}H^{132}N^8O^{24}$ , homologous with tetracodeine (p. 372). No dimorphine is produced, although dicodeine is easily formed under similar circumstances. These results show that the so-called sulphomorphide is really the sulphate of tetracodeine.

When trimorphine hydrochloride is dissolved in strong hydrochloric acid, and the whole kept at  $100^\circ$  for eight hours, a change is produced indicated by the reaction—



The acid liquid, when diluted with water, neutralised with caustic soda, and precipitated with sodium carbonate, yields a white precipitate, for the most part soluble in ether; and the ethereal solution, agitated with a few drops of hydrochloric acid, gives a viscid liquid which wholly refuses to crystallise, and accordingly does not appear to contain any appreciable quantity of apomorphine. On leaving it over sulphuric acid, a brittle gum was obtained which, after heating to  $100^\circ$ , exhibited the composition  $C^{122}H^{132}N^8O^{24}.6HCl$ , which is that of the hydrochloride of a base formed from trimorphine by substitution of  $Cl^2$  for  $(HO)^2$ .

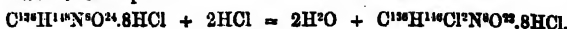
The occurrence of this reaction in the substance which evidently corresponds in the morphine series with the polymeride provisionally viewed as *tricodeine* in the codeine series (p. 372), corroborates the view that these substances are actually the threefold polymerides of morphine and codeine respectively. The action of hydrochloric acid on tricodeine is a simple dehydration (see above),



whereas that on trimorphine is of an entirely different character, the elements of  $HCl$  being added on, as well as those of  $H^2O$  subtracted (see above).

Tetramorphine, heated with hydrochloric acid, does not undergo any transformation,

but simply forms the hydrochloride  $C^{12}H^{12}N^2O^2, 8HCl$ . In this respect it resembles tetracodeine, but differs from diapotetramorphine, which undergoes a transformation similar to that of trimorphine:



2. **Polymerisation by the action of Phosphoric acid** (Wright, *Chem. Soc. J.*, [2], x. 652). Phosphoric acid acts on morphine in the same manner as on codeine (p. 372), excepting that the resulting polymerides of morphine are converted by abstraction of water into apo-derivatives.\*

When 1 part of morphine is treated with phosphoric acid solution (3 glacial acid to 5 water), and the liquid gently boiled until the boiling-point rises to  $180^{\circ}$ – $190^{\circ}$ , a brown liquid is obtained which, when diluted with water, gives an immediate amorphous precipitate with excess of sodium carbonate; the filtrate from this, if quickly separated, contains unchanged morphine, which gradually crystallises out on standing. This precipitate is purified by solution in hydrochloric acid, reprecipitation by sodium carbonate, and rapid filtration; other extracts a very small quantity (less than 0.6 p.c.) of a base soluble in that liquid; on agitation with hydrochloric acid, anhydrous crystals are obtained which present all the appearances and reactions of the hydrochloride of apomorphine,  $C^{12}H^{12}N^2O^2, 2HCl$ .

The formula here given to apomorphine, which is double of that originally assigned to it (1st Suppl. 839), appears to be justified by a comparison of the results of the action of phosphoric and sulphuric acids on morphine and codeine, the apomorphine being in all probability derived by dehydration from the previously formed dimorphine, by the reaction:



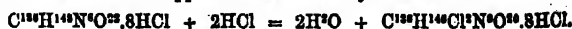
Comparison of the physical properties of apomorphine and its salts with those of the different polymerides of codeine, likewise indicates a greater analogy to diocodeine than to codeine itself, or to tetracodeine. The systematic name of apomorphine is accordingly tetraapo-dimorphine.

The portion of the precipitate produced by sodium carbonate, which is insoluble in ether, oxidises by exposure to air with great rapidity; dissolved in hydrochloric acid, and fractionally precipitated by sodium carbonate, it finally yields a light fawn-coloured precipitate, which rapidly darkens and absorbs oxygen while drying. Washed and dried as rapidly as possible, it gave numbers agreeing with the formula  $C^{12}H^{12}N^2O^{12}$ . Wright, however, supposes that of the 40 atoms of oxygen, 18 were derived from atmospheric oxidation, and that the true formula of the recently formed base is  $C^{12}H^{12}N^2O^{22}$ . According to this view it is diapo-tetramorphine, formed by the reaction:



This base exerts upon dogs an emetic action quite as powerful as that of apomorphine, but does not appear to produce so much after-depression.

**Action of Hydrochloric acid on Diapo-tetramorphine.**—When freshly prepared diapo-tetramorphine (unoxidised) is dissolved in a large excess of strong warm hydrochloric acid, the solution boiled down gently, almost to dryness, and finally evaporated to dryness on the water-bath, a tarry residue is obtained, readily soluble in water; addition of strong hydrochloric acid to this aqueous solution throws down flakes of the hydrochloride of a new base which is obtained in greatest purity by fractional precipitation with strong hydrochloric acid; and the last precipitate being washed with weak acid, and dried at  $100^{\circ}$ , yields a brownish, tarry, brittle mass, much resembling the hydrochloride of chlorotetramorphine (p. 370), and having the composition  $C^{12}H^{12}Cl^2N^2O^{22}, 8HCl$ . It appears to be formed by the reaction:



In physical and chemical properties this substance much resembles chlorotetramorphine, from which it differs in composition by  $-H^2O$ ; sodium carbonate throws down from its aqueous solution fawn-coloured flakes, almost wholly insoluble in ether, and darkening by exposure to air; like all the other 'tetra' bases it yields a blood-red colour on warming with an acid solution of silver nitrate.

**Action of Hydriodic acid and Phosphorus on Diapo-tetramorphine.**—When freshly prepared unoxidised diapo-tetramorphine is dissolved in dilute hydriodic acid by the aid of heat, and the solution gently boiled down with the addition of excess of hydriodic acid and a piece of phosphorus, till the boiling-point rises to  $125^{\circ}$ , a viscous liquid is obtained, from which, on filtration through asbestos and precipitation by water, a

\* The prefix *apo* may be conveniently used to designate generally the removal of the elements of  $H^2O$ ; *diapo*, for the removal of  $2H^2O$ ; *tetraapo*, for  $4H^2O$ , and so on.

substance may be obtained undistinguishable in appearance from the similar body resulting from analogous treatment of tetracodeine (p. 373), and having the composition  $C^{136}H^{116}I^{16}N^{10}O^{22}.8HI$ . It is produced by the reaction:



which is perfectly parallel with the reaction with hydrochloric acid (*infra*) and with the action of hydriodic acid and phosphorus on tetracodeine (methyl being eliminated in the latter case):



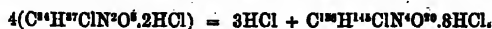
When heated it leaves a very difficultly combustible charcoal. With nitric acid and silver nitrate it strikes a blood-red colour.

3. **Polymerisation by the action of Zinc Chloride** (Mayer a. Wright, *Chem. Soc. J.* [2], xi. 211). When morphine hydrochloride is heated for a short time with a concentrated solution of zinc chloride, a crystalline compound of the two is obtained, from which, by repeated solution in water and crystallisation, the zinc chloride may be removed, the morphine hydrochloride remaining undissolved. But if the heating be continued, there are formed, according to the temperature and duration of the action, the hydrochlorides of the following bases:

- |  |                                     |
|--|-------------------------------------|
| A. <i>Tetrapodimorphine</i> (apomorphine) . . . . .  | $C^{608}H^{384}N^{10}.4HCl$         |
| B. A chlorinated base, soluble in ether, and yielding<br>an uncrystallisable hydrochloride . . . . .   | $C^{84}H^{72}ClN^{10}O^{22}.2HCl$   |
| C. <i>Octapotetramorphine</i> , polymeric with apomor-<br>phine, insoluble in ether, and yielding an un-<br>crystallisable hydrochloride . . . . . | $C^{1136}H^{1136}N^{10}O^{16}.8HCl$ |
| D. A chlorinated base, insoluble in ether, and yield-<br>ing an uncrystallisable hydrochloride . . . . .   | $C^{136}H^{116}ClN^{10}O^{22}.8HCl$ |
| E. A base probably isomeric with apomorphine, or<br>perhaps impure apomorphine.  |                                     |

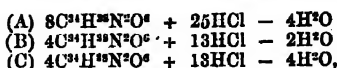
The apomorphine is formed when the mass is kept at a temperature of  $120^{\circ}$ – $125^{\circ}$  for more than twenty minutes, the yield being larger the lower the temperature between these limits, and the more concentrated the solution of zinc chloride. The base F, isomeric with apomorphine, but differing from it by forming an unstable platinum-chloride, and the chlorinated base B, were formed after treatment for an hour at  $170^{\circ}$ . *Octapotetramorphine* (C) was produced when nearly equal volumes of solid zinc chloride, strong hydrochloric acid, and morphine, were heated together in sealed tubes to  $180^{\circ}$ – $220^{\circ}$  for 24 hours. Its hydrochloride is much like those of chlorotetramorphine and bromotetramorphine, but has a darker colour; it is insoluble in absolute but soluble in dilute alcohol; with nitric acid it gives a dirty-red colour, and with sodium carbonate an amorphous precipitate almost insoluble in ether. This base differs strikingly from apomorphine in being destitute of emetic properties.

The chlorinated base, D, is formed by prolonged exposure of the mixture to a lower temperature (36–48 hours at  $100^{\circ}$ ). Its hydrochloride yielded, with sodium carbonate, a precipitate insoluble in ether and only sparingly soluble in chloroform. If it is a single substance, it may be regarded as formed from the chlorinated base, B, by polymerisation and abstraction of the elements of hydrogen chloride—

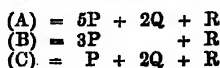


4. **Polymerisation by the action of Hydrochloric Acid.** The experiments of Matthiessen a. Wright have shown that when hydrochloric acid acts on morphine in sealed tubes at  $140^{\circ}$ – $150^{\circ}$ , apomorphine is produced (*1st Suppl.* 839). Other products are, however, formed at the same time, varying in composition according to the temperature, the proportions of the materials used, and the duration of the action. The following have been obtained:—(A) By heating morphine in a flask on the water-bath for six hours with 5–6 times its weight of strong hydrochloric acid, then diluting with water, nearly neutralising with caustic soda, precipitating with sodium carbonate, dissolving the precipitate in ether, and agitating the ethereal solution with a few drops of hydrochloric acid. (B) By heating morphine as in A for five hours, and evaporating on the water-bath in an open basin for four hours, more. (C) By gently boiling morphine with about 6 parts of hydrochloric acid for four hours, the product being treated as in A.

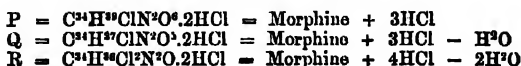
The analyses of these products leads to the following formulae—



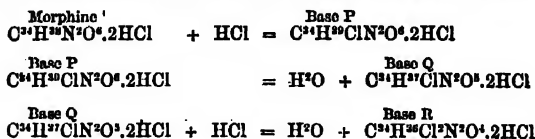
which are those required for mixtures of bases denoted by the formulae—



where—

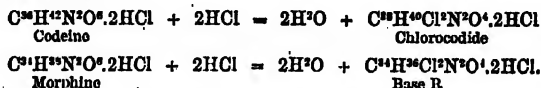


whence it is considered probable that the following reactions take place—



i.e., that the elements of HCl become added on to morphine *previously* to the abstraction of the elements of H<sup>2</sup>O, a reaction similar to that which takes place in the case of several codeine derivatives (p. 371).

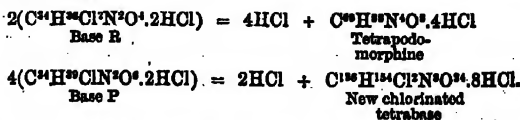
The last-formed base, R, is homologous with chlorocodide (p. 369), the reactions which express the formation of the two bases from morphine and codeine respectively being precisely similar—



Now as chlorocodide reproduces ordinary codeine by the action of water (1st Suppl. 481), it is evident that no polymerisation has taken place during its formation; and as its formation appears to be *preceded* by the formation of a base homologous with base P, it follows that the formula of codeine must be written C<sup>14</sup>H<sup>10</sup>N<sup>2</sup>O<sup>4</sup>, instead of the half of this, as formerly, while by analogy morphine must be written C<sup>14</sup>H<sup>10</sup>N<sup>2</sup>O<sup>4</sup>, a result in accordance with the composition of mono-acetyl-morphine (p. 819).

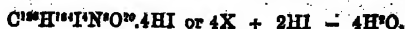
Base Q is no doubt identical with the body of the same composition obtained by the action of zinc chloride on morphine.

When the action of hydrochloric acid on morphine is continued beyond the point reached in C, apomorphine hydrochloride is produced, together with the hydrochloride of a chlorinated tetrabase, C<sup>14</sup>H<sup>14</sup>Cl<sup>2</sup>N<sup>2</sup>O<sup>4</sup>. These bases are probably formed by polymerisation of the bases P and R, and subsequent elimination of the elements of hydrogen chloride: thus—



This view is corroborated by the fact that when the mixture of P and R obtained in experiment B was gently boiled with hydrochloric acid for two hours, apomorphine and the chlorinated base were produced in considerable quantity.

**5. Polymerisation by the action of Hydriodic Acid in presence of phosphorus** (Wright, *Chem. Cent.* 1872, 313). When morphine is heated with about four times its weight of aqueous hydriodic acid (containing 54–55 p.c. HI), the liquid becomes brown from separation of iodine; but if phosphorus be then added, the colour disappears, and a syrupy liquid is obtained, which, when treated in the same manner as in the corresponding codeine reaction (p. 371), yields a product having the composition—





where X denotes the hypothetical base,  $C^{14}H^{12}N^2O^2$ ; and the reaction takes place according to the equation—



This product closely resembles that which is obtained in like manner from codeine. Heated for about 5 hours with about 300 times its weight of water, it yields, by elimination of 2HI, the compound  $C^{14}H^{12}I^2N^2O^2 \cdot 8HI$ . If this product be further treated with water, one half of the basic iodine is again eliminated as HI, yielding



All these iodised derivatives of morphine resemble the corresponding codeine derivatives in chemical properties and in physiological action.

The table on p. 826 exhibits the relations to morphine and its polymerides of the derivatives above described, such derivatives being actually derived from morphine as starting point; several bodies derived from codeine as starting point, and also belonging to one or other of these series, are tabulated under CODEINE (p. 375). In this, as in the preceding table, the symbols  $M$ ,  $M^2$ ,  $M^3$ ,  $M^4$ , are applied respectively to morphine, dimorphine (hypothetical), trimorphine, and tetramorphine. Each of these bases forms a hydrochloride (and probably other analogous salts) in which the number of molecules of HCl associated in the salt with the base is equal to the number of nitrogen-atoms in the molecule of the base, i.e., two for derivatives from morphine, four for those from dimorphine, six from trimorphine, and eight from tetramorphine.

Another class of bases included in the table, and designated as the *tetrahydro-series*, is formed by the derivatives obtained by the joint action of hydriodic acid and phosphorus on morphine; these may be all viewed as derived from a hypothetical base related to tetramorphine, and containing  $H^{10}$  more in its molecule than that substance; or, what amounts to the same thing, from the tetra-polymeride of a base containing  $H^4$  more than morphine, i.e. having the formula  $(C^{14}H^{12}N^2O^2)^4 = (M + H^4)^4$ .

**Oxidation of Morphine Derivatives.** When apomorphine hydrochloride is heated with excess of potash-ley, the base, which is at first precipitated, redissolves, and the solution quickly turns brown in consequence of absorption of oxygen from the air. By agitation with ether, after neutralisation with hydrochloric acid, a peculiar colouring matter is extracted, which imparts to the ether a fine purple-violet tint, affording a good test for the presence of apomorphine. On agitating the ethereal solution with an alkali, a grass-green watery layer separates, from which hydrochloric acid precipitates indigo-blue flakes insoluble in water and in acids, but soluble in alkalis with green colour, in water containing ammoniacal salts with light blue colour, and in alcohol, benzene, carbon sulphide, ether and chloroform with various shades of purple and violet. Especially remarkable are the variations in the depth of colour produced by equal quantities of this substance in equal volumes of different solvents. The analysis of the purified blue precipitate led to the empirical formula,  $C^{14}H^{12}N^2O^2$ . No means have, however, been yet discovered of fixing its molecular weight; it does not unite either with acids or with bases; its neutral ammoniacal solution, prepared by dissolving it in aqueous ammonia, and leaving the solution for some days over sulphuric acid, gives no precipitates with silver nitrate, lead acetate, barium nitrate, &c.; with mercuric chloride, however, it forms a dark-brown precipitate containing chlorine and a large quantity of mercury, and probably consisting of a mixture of calomel with the mercury salt of some oxidation-product of the blue compound.

Diapodimorphine and deoxymorphine treated in like manner likewise yield the blue compound, but it is not produced from the monomorphine derivatives, or from any derivative of the tetra-series (Mayer a. Wright, *Chem. Soc. J.* [2], xi. 1082).

**Action of Heat on Morphine Derivatives.** The hydrochlorides of the monomorphine derivatives are decomposed by gradual heating to  $150^\circ$ – $180^\circ$ , and the products mixed with caustic potash and distilled yield pyridine, together with small quantities of methylamine, the latter probably arising from decomposition of a polymerised base formed during the reaction. The tetra-derivatives treated in like manner yield methylamine but no pyridine, and the di-derivatives yield no volatile bases whatever. These results indicate a different relation of the nitrogen to the other elements in the several polymeric groups (Mayer a. Wright, *Chem. Soc. J.* [2], xi. 1086).

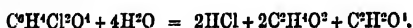
## DERIVATIVES AND POLYMERIDES OF MORPHINE.

Name	Origin	Formula	Relation to Morphine or polymerides thereof
<i>Mono-Series.</i>			
Morphine	—	$C^{17}H^{19}N^3O^6$	$\bar{M}^1 + HCl$
'Base P'	Morphine and hydrochloric acid	$C^{17}H^{19}ClN^3O^6$	$\bar{M}^1 + HCl - H^2O$
'Base Q'	" also morphine and zinc chloride	$C^{17}H^{19}Cl_2N^3O^6$	$\bar{M}^1 + 2HCl - 2H^2O$
'Base R'	Morphine and hydrochloric acid (homologous to 'chlorocodide')	$C^{17}H^{19}Cl_2N^3O^6$	
<i>Di-Series.</i>			
Dimorphine (hypothetical)	—	$C^{34}H^{38}N^4O^{12}$	$\bar{M}^2$
'Apomorphine' (tetrapodimorphine)	Morphine and hydrochloric acid	$C^{34}H^{38}N^4O^{12}$	$\bar{M}^2 - 4H^2O$
	" sulphuric acid		
	" phosphoric acid		
	" zinc chloride		
<i>Tri-Series.</i>			
Trimorphine	Morphine and sulphuric acid	$C^{51}H^{54}N^6O^{18}$	$\bar{M}^3$
	Trimorphine and hydrochloric acid	$C^{51}H^{54}Cl_3N^6O^{18}$	$\bar{M}^3 + 2HCl - 2H^2O$
<i>Tetra-Series.</i>			
Tetramorphine	Morphine and sulphuric acid	$C^{68}H^{72}N^8O^{24}$	$\bar{M}^4$
	hydrochloric acid	$C^{68}H^{72}Cl_4N^8O^{24}$	$\bar{M}^4 + 2HCl$
	"	$C^{68}H^{72}N^8O^{24}$	$\bar{M}^4 - 2H^2O$
Diapetetramorphine	" phosphoric acid	$C^{68}H^{72}Cl_2N^8O^{24}$	$\bar{M}^4 + HCl - 4H^2O$
	" zinc chloride	$C^{68}H^{72}N^8O^{18}$	$\bar{M}^4 - 8H^2O$
	"	$C^{68}H^{72}Cl_2N^8O^{24}$	$\bar{M}^4 + 2HCl - 4H^2O$
Octapetetramorphine	Diapetetramorphine and hydrochloric acid	$C^{68}H^{72}Cl_4N^8O^{24}$	$\bar{M}^4 + 2HCl - 4H^2O$
	" hydrochloric acid	$C^{68}H^{72}Cl_4N^8O^{24}$	$\bar{M}^4 + H^2O$
<i>Tetra-hydro-Series.</i>			
Hypothetical tetrapolymerides of $\bar{M}^1 + H^1$	Morphine, hydriodic acid, and phosphorus	$C^{68}H^{140}IN^8O^{24}$	$(\bar{M}^1 + H^1) + 4HI - 4H^2O$
	Action of water on above	$C^{68}H^{140}IN^8O^{24}$	$(\bar{M}^1 + H^1) + 2HI - 4H^2O$
	Further "	$C^{68}H^{140}IN^8O^{24}$	$(\bar{M}^1 + H^1) + HI - 4H^2O$

**MOSCHATIN.** A nitrogenous substance contained in the Iva plant (*Achillea moschata*; see *ACHILLEA*, p. 21).

**MUCIO ACID,  $C^8H^{10}O^4$**  (Lamprecht, *Ann. Ch. Pharm.* clxv. 253). *Normal ethyl mucate,  $C^8H^{14}(C^2H^5)^2O^6$* , is not formed by the action of hydrochloric acid or sulphuric acid on a mixture of mucic acid and alcohol, and can only be obtained by Malaguti's method; i.e., by heating mucic acid with sulphuric acid until the mass blackens, and adding alcohol to it after 12 hours' standing. The crystalline product is again allowed to stand for 24 hours, then washed with cold alcohol, and recrystallised from hot alcohol; it melts at  $158^\circ$ . By boiling with water it is decomposed, mucic acid separating out. Hot alcohol also decomposes it partially, with formation of the acid ether,  $C^8H^{10}O^4(C^2H^5)$ , which remains in the mother-liquor. It crystallises in white silky needles containing 3 mol. of water, and is readily soluble in alcohol and water; at  $100^\circ$  the water escapes, and the ether melts to a glassy hygroscopic mass. When the normal ether is carefully heated in a retort, alcohol distils over, and an amber-coloured mass is left behind, which is readily soluble in water, the solution containing mucic acid. On heating it gradually to  $240^\circ$ , the distillate contains water, alcohol, pyromucic acid, and a volatile crystalline substance, which is insoluble in hot water. The residue forms a black humus-like mass dissolving in alkalis.

**Chloromucic Acid,  $C^8H^7ClO^4$** . This acid, which was discovered by Liéboldart (iii. 1058), and afterwards investigated by Bode and Wichelhaus (v. 1093), is obtained by heating mucic acid with phosphorus pentachloride and decomposing the product with water.\* It forms long white needles, dissolving readily in alcohol and ether, and in 19 parts of boiling water, but only very sparingly in cold water; it is a bibasic acid. When it is heated, a small quantity sublimes, but the greater part undergoes decomposition. Bromine does not act on it in presence of water at a gentle heat, but by heating the substances in closed tubes, a great quantity of carbon dioxide is formed, together with a crystalline compound and an oily liquid smelling like pepper. Alcoholic potash acts but slowly on the acid; below  $190^\circ$  a large quantity remains unaltered, whilst above  $200^\circ$  a most violent explosion takes place. By keeping the temperature between these limits, the acid is resolved into hydrochloric acid, acetic acid, and oxalic acid:—



**Hydromucic Acid,  $C^8H^9O^4$** . This compound, which has been already described by Bode and Wichelhaus, and by Schmelz n. Beilstein (iv. 764), under the name of *mucic acid*, is produced by the action of sodium-amalgam and water on chloromucic acid. It is a bibasic acid, forming long white needles, melting at  $195^\circ$  and dissolving readily in alcohol and hot water, but only sparingly in cold water.

**Bromhydromucic Acid,  $C^8H^7BrO^4 + H^2O$** , is formed by dissolving 1 mol. of hydromucic acid in hot water and adding 1 mol. of bromine. It forms white, shining, hard prisms, melting at  $183^\circ$ ; it is easily decomposed by heat, and dissolves readily in hot, but sparingly in cold water; on evaporating the aqueous solution on a water-bath, hydrobromic acid is given off.

**Oxyhydromucic Acid,  $C^8H^9O^5$** , is produced by adding freshly precipitated silver oxide to an aqueous solution of bromhydromucic acid. It is readily soluble in water, alcohol, and ether, and crystallises with difficulty. It volatilizes without decomposition. The *barium salt*,  $C^8H^7BaO^6 + 2H^2O$ , is precipitated from a concentrated aqueous solution by absolute alcohol, as a crystalline powder which gives off part of its water at  $105^\circ$ , being converted into  $2C^8H^7BaO^6 + H^2O$ .

The mother-liquors of bromhydromucic acid contain dibromadic acid,  $C^8H^7Br^2O^4$ , which by the action of moist silver oxide is converted into dioxynadic acid,  $C^8H^{10}O^4$ ; and by heating hydromucic acid with bromine and water in different proportions, tribromadic acid,  $C^8H^7Br^3O^4$ , and tetrabromadic acid,  $C^8H^7Br^4O^4$ , are produced, the former of which is converted by moist silver oxide into trioxynadic acid,  $C^8H^{10}O^5$  (see *ADIPIC ACID*, p. 28).

**Mucic Acid,  $C^8H^{10}O^4$** , is obtained by adding silver oxide to a hot solution of isodibromadic acid (formed by adding bromine to a warm solution of hydromucic acid in glacial acetic acid) and decomposing the resulting silver salt with hydrochloric or sulphuric acid. It forms large, apparently monoclinic, crystals, melting above  $100^\circ$ , and dissolving freely in water, alcohol, and ether. The *barium salt*,  $(C^8H^{10}O^4)Ba + 4H^2O$ , forms warty crystals and is freely soluble in water, but not in alcohol. The *sodium salt* forms a syrup; the *ammonium salt* gives a white precipitate with

\* According to Ador (*Dest. Chem. Ges. Ber.* iv. 827) the product is considerably increased by addition of phosphorus oxychloride to the pentachloride.

silver nitrate, and its aqueous solution becomes acid on evaporation. When mucous acid is heated for some time to 100°, or a little higher, carbon dioxide is evolved and the residue assumes a dark colour. By boiling the acid with baryta-water it yields carbon dioxide, acetic acid, succinic acid, and another acid which could not be obtained in the pure state.

**Mucobromic Acid**,  $C^4H^2Br^2O^3$ . This acid, discovered by Schmelz a. Beilstein (iv. 763), is obtained by adding bromine in excess to pyromucic acid in presence of water—



It crystallises in shining white plates, melting at 120°–130°, and dissolves readily in ether, alcohol, and hot water, but only sparingly in cold water.

One mol. mucobromic acid heated with 3 mol. bromine and water in closed tubes to 120°–130°, yields tribromomethylene dibromide and hexabromethane, together with compounds isomeric or identical with dibromofumaric acid and tetrabromobutyric acid.

**Dibromofumaric Acid**,  $C^4H^2Br^2O^4$ , forms warty crystals melting at 108°–120°; on heating it in a current of carbon dioxide to 100°–105°, the anhydride,  $C^4H^2Br^2O^3$ , sublimes in needles, melting at 95°–120°, and volatilising readily at 70°, and at the common temperature *in vacuo*. On dissolving the anhydride in cold baryta-water, and evaporating the solution over sulphuric acid, the salt,  $C^4H^2Br^2O^3Ba + 2H^2O$ , crystallises in fine plates. The mother-liquor gives with alcohol a crystalline precipitate,  $C^4H^2Br^2O^3Ba + H^2O$ . The aqueous solution of the barium salt gives with silver nitrate a white explosive precipitate.

**Tetrabromobutyric Acid**,  $C^4H^2Br^4O^3$ , crystallises from a hot aqueous solution in transparent oblique plates, melting at 115°, and dissolving but sparingly in cold water.

**Tribromomethylene dibromide**,  $C^2HBr^2$ , crystallises from alcohol in long, brittle needles, melting at 50°–52°; on heating it with alcoholic potash, it is converted into *tetrabromomethylene*,  $C^2Br^4$ , crystallising in thin plates melting at 50°. **Hexabromethane**,  $C^2Hr^6$ , forms thick colourless prisms which are insoluble in alcohol, and decompose at 170° (Limprecht).

**MUCIN.** Mucin from the submaxillary gland has been examined by J. Obolensky (*Med.-Chem. Untersuchungen*, 1871, 590). It was prepared as follows. The salivary glands of the ox were cleaned as much as possible, and finely rubbed down with pounded glass. The mass was placed in water and allowed to stand over-night, then filtered, the residue being again treated in the same manner. The filtrate was precipitated by excess of acetic acid, and the precipitate was well washed with water and a little acetic acid, afterwards with warm alcohol, and then dried. This substance, insoluble in acetic acid, is obtained only from the submaxillary gland, the parotid yielding only albuminoids (globulin). The glands contain none of the substance described by Miescher as nuclein.

Dry mucin gives 2.44 p.c. of pure ash, of which 1.64 parts are soluble in water, the rest in hydrochloric acid. Mucin contains no sulphur. The amount of phosphoric acid (1.06–1.07 p.c.) agrees with the quantity of ash. Mucin free from ash has a composition (the mean of two analyses) 52.2 C., 7.18 H., 11.87 N., 28.75 O. This agrees very nearly with Scherer's analysis of mucin from a cystin fluid, viz., 52 C., 7.0 H., 12.6 N., 28.2 O. It differs from Eichwald's analysis (48.9 C., 6.8 H., 8.6 N., 35.8 O.) chiefly in the amount of nitrogen.

Freshly precipitated and moist mucin swells readily in water, is easily soluble in lime- and baryta-water, not precipitated by tannic acid, ferric chloride, or mercuric chloride. It is soluble in concentrated hydrochloric and nitric acid, also in sodium carbonate. When mucin is treated with hot alcohol and dried on the water-bath, it scarcely swells in water, and is very slowly soluble in lime- or baryta-water, or soda solution. The solutions behave like the former in regard to the above-mentioned reagents.

Dried and pulverised mucin, heated for 25 minutes with dilute sulphuric acid, is partly dissolved, and gives, with excess of caustic soda and copper sulphate, a red precipitate of cuprous oxide. If it be heated for a longer time, the quantity of reducing agent diminishes, and ultimately disappears. This fact, and the insolubility of the reducing agent in absolute alcohol, show that it is not identical either with grape sugar or milk-sugar.

**MULBERRY-LEAVES.** E. Reichenbach (*Ann. Ch. Pharm.* cxlii. 46) has examined the composition of mulberry-leaves from different countries with reference to the view, suggested by Liebig, that the silkworm disease which prevails in Europe but not in China or Japan, has its origin in deficient or unsuitable nourishment. The following table gives the results of his analyses for 1,000 parts of the dry leaves.

Mulberry-leaves from	Nitrogen	Protein substance	Ash free from carbon	K <sub>2</sub> O	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	NaCl
Japan . . .	32.8	201	125.9	30.02	37.93	7.35	7.99	41.11	3.41
" . . .	33.6	210	135.8	32.74	40.11	7.61	7.31	45.13	4.06
China . . .	31.3	195	135.8	32.01	37.42	10.25	6.57	47.23	6.57
Piedmont . . .	23.4	146	141.7	34.14	51.04	5.61	5.65	47.58	2.25
" . . .	23.4	146	144.5	23.84	51.90	5.14	5.07	54.36	2.96
" . . .	24.9	155	146.7	24.04	52.84	4.45	6.30	51.74	2.38
Alais (France) . . .	23.8	148	110.6	33.17	48.37	5.25	6.25	24.24	2.96
Brescia . . .	33.6	210	113.4	26.90	34.98	6.88	8.77	20.32	2.55

From these numbers Liebig and Reichenbach conclude that French and Italian mulberry-leaves, on account of their comparative poorness in nitrogenous constituents, do not afford sufficient nourishment for the silkworms imported from China and Japan, which are accustomed to a more nutritive fodder.

In mulberry-leaves from Turkestan, where also the silkworms are free from disease, Reichenbach found from 3.38 to 4.05 (average 3.73) p.c. nitrogen, which is equivalent to 211–253 lbs. of protein substance in 1,000 lbs. of leaves (*Ann. Ch. Pharm.* civiii. 92; *Chem. Soc. J.* [2], ix. 435).

On the other hand, Sestini (*Landwirth. Versuchs-Stationen*, xv. 286) finds that the leaves of mulberry-trees grown at Friaul in Italy contain a larger proportion of nitrogen than those from China, Japan, or Turkestan. The trees had all been manured with dung, and were usually stripped of leaves every second year. The following table shows the percentage of water in the fresh leaves, and of organic matter, ash, and nitrogen in the dry leaves; also the composition of the ash at various stages of growth:—

Mulberries	<i>Morus alba silvatica</i>				<i>Morus alba domestica</i>				Chinese mulberries	Improved native
	April 28	May 8	May 12	May 17	April 29	May 8	May 12	May 17	August 24	August 24
Water . . .	75.6	71.3	66.7	62.2	78.1	73.6	70.1	69.4	72.4	66.9
Organic matter . . .	91.8	92.3	93.1	91.5	91.7	92.8	92.9	92.8	91.7	71.6
Ash . . .	8.2	7.7	6.9	8.5	8.3	7.2	7.1	7.2	8.3	28.4
Nitrogen . . .	6.1	5.3	4.6	3.8	6.1	4.6	4.6	5.6	4.1	5.1
Silica . . .	9.4	10.6	10.7	11.6	9.6	10.4	10.8	15.2	8.0	15.9
Lime . . .	21.1	24.6	26.0	28.3	24.3	26.3	27.6	28.9	31.7	33.3
Magnesia . . .	7.6	9.7	9.0	8.8	7.5	8.2	8.0	7.9	11.2	10.7
Alkali . . .	15.6	17.1	16.9	19.0	16.6	17.9	18.2	19.2	24.1	16.0
Sulphuric acid . . .	1.8	1.6	1.8	2.1	2.0	2.5	2.9	2.9	1.3	1.3
Phosphoric acid . . .	2.4	2.7	2.0	1.6	2.0	1.9	1.8	1.5	18.1	12.1
Chlorine . . .	2.1	1.7	1.2	1.1	1.6	1.3	1.3	1.1	7	0.9
Undetermined, and loss . . .	17.6	13.0	14.4	12.2	18.3	13.8	13.1	11.3	4.9	0.8

**MUSCARINE** (Schmiedberg & Poppe, *Deut. Chem. Ges. Ber.* iii. 281; Ruckert, *N. Rep. Pharm.* xxi. 193). An alkaloid of unknown composition contained in the hyacinth (*Agaricus muscarius*). To prepare it, the alcoholic extract of the evaporated juice is dissolved in water; the solution precipitated with basic lead acetate and ammonia; the filtered liquid is evaporated to dryness; the residue again dissolved, and the solution treated with basic lead acetate and ammonia; the filtrate, after concentration to a syrup, is mixed with excess of lead hydrate and evaporated down to expel the ammonia; the residue exhausted with absolute alcohol, the filtrate evaporated, and the residue dissolved in water; the bases are converted into sulphates, which are shaken with ether to remove acetic acid; the ether evaporated; barium hydrate added in sufficient quantity to leave the solution slightly acid; and the muscarine precipitated either with potassium-mercury iodide or with potassium-bismuth iodide. If the

former reagent is employed, the precipitate is washed on a filter with water containing sulphuric acid, then suspended in water; an equal volume of moist barium hydrate is added; and the liquid is treated with hydrogen sulphide, and the filtrate with silver sulphate. After another filtration the liquid contains nothing but muscarine, together with the silver salt, which is easily removed. When potassium-bismuth iodide is used, the product is larger but less pure (Schmiedberg a. Poppe). Ruckert finds that when potassium-mercury iodide is employed, a kilogram of thick extract yields from 7 to 8 decigrams of muscarine sulphate.

Muscarine forms a colourless or yellowish syrupy substance, without taste or smell, soluble in all proportions of water and alcohol, insoluble in ether, and only sparingly soluble in chloroform; it becomes crystalline over sulphuric acid, but is very deliquescent. It has a strong alkaline reaction, and precipitates iron and copper salts; boiling for 5-10 minutes with potash-ley or diluted sulphuric acid has no apparent action on it; heated with moist solid potash, it evolves ammoniacal vapours having a fishy odour, no browning taking place until the heat has been continued for some time. Manganese dioxide and sulphuric acid, chlorine-water, permanganate of potassium, and a mixture of potassium chromate and sulphuric acid, produce no coloration, the oxidising agents being, however, reduced. Excess of bromine-water gives a yellow precipitate, soon redissolving, and forming a yellow solution which soon becomes colourless.

Mercury-potassium iodide and bismuth-potassium iodide give amorphous precipitates, becoming crystalline on standing; gold chloride yields a non-crystalline precipitate, while mercury chloride yields crystals on long standing; platonic chloride, potassium ferrocyanide, potassium platino-cyanide and tannin do not precipitate the sulphate. This salt is deliquescent, and crystallises by evaporation over sulphuric acid.

Muscarine is a strong narcotic poison, and is antagonistic in its action to atropine.

**MUSCULAR TISSUE.** (Pick a. Wislicenus, *Phil. Mag.* xxxi. 486; Parkes, *Proc. Roy. Soc.* xv. 339, xvi. 44; Pettenkofer a. Voit, *Zeitschr. f. Biologie*, ii. 566; *Chem. Centr.* 1867, 790; *Sitz. d. k. Bayer. Akad. d. Wiss.* 1867, i. 364; M'Donnell, *Obs. on the Functions of the Liver*, Dublin, 1865; O. Nasse, *Beiträge z. Phys. d. contractilen Substanz*, *Arch. f. d. Ges. Phys.* ii. 97; L. Hermann, *Unters. über die Stoffwech. d. Muskeln*, Berlin, 1867). The nature of the chemical changes which give rise to muscular energy can hardly be yet considered as fully elucidated, though we are in a position to make some pretty positive statements on the subject. It would appear that the older idea, that the combustion of some nitrogenous substance was the source of muscular work must be definitely abandoned, or at least must be understood in a very different sense from that in which it was formerly accepted. Pick a. Wislicenus, Parkes, and others, have proved that the nitrogen excreted from the body during muscular work and some hours after it, is, even when its energy of combustion is calculated as high as possible, quite insufficient to account for the work done (see *1st Suppl. NUTRITION*, p. 874); and Naurocki (*Beiträge z. Stoffwech. im Muskel*; *Central. f. d. Med. Wiss.* 385), Voit, &c., have shown that the products of nitrogenous waste (creatine, creatinine, &c.) are not increased in tetanised muscles. We are thus reduced for a starting-point to the old observation that the venous blood which leaves a contracting muscle contains more carbonic anhydride and less oxygen than that leaving a resting muscle, and are led to suspect that whatever changes may occur in the proteid matters of a contracting muscle, the substances which the muscle loses by its contraction contain no nitrogen. M'Donnell has shown that muscular tissue contains glycogen, and that this, during contraction, is converted into glucose; and Nasse, who confirms this, also finds that the total quantity of glycogen and dextrose in a muscle in a state of *rigor mortis* is less than that in muscle killed without stiffening; and this gains importance from the fact that, as we shall hereafter see, *rigor mortis* and muscular contraction are probably fundamentally of the same nature; however, the quantity of carbon which disappears in the form of the above compounds is not sufficient to account for that in the sarco-lactic acid which is formed at the same time, so that the observation does not, by itself, go for much.

Hermann, by a series of most careful analyses and estimations of the gases evolved by frogs' muscles under different conditions, has thrown much light on the chemical processes which occur during muscular contraction and also on the nature of *rigor mortis*, and, as the result of his experiments, has put forward a theory which seems to unite previous observations in a consistent manner. He shows first that the evolution of carbonic anhydride and the taking up of oxygen, though they go on side by side in a contracting muscle in the body, are yet quite independent processes; a living muscle, deprived of blood, gives off in a vacuum a certain amount of carbonic anhydride and some nitrogen, but no oxygen whatever; but although it is thus shown to contain no free oxygen, yet, if it be made to contract or be thrown into a state of *rigor mortis*, it

will give off a large additional quantity of carbonic anhydride, while at the same time sarco-lactic acid forms in it. Moreover, if a muscle be tetanised as long as it will contract, the total quantity of carbonic anhydride given off by it is less than that which would have been given off by throwing the muscle directly into *rigor mortis*; but if this latter condition be induced after the tetanisation, exactly the missing quantity of carbonic anhydride is evolved. We must therefore conclude that a living muscle contains a definite store of some unknown substance which yields carbonic anhydride and sarco-lactic acid, and that the breaking up of this substance lies at the base of both muscular contraction and *rigor mortis*; and, further, that the process can go on quite independently of any simultaneous taking up of oxygen. When the experiments were repeated in a gaseous mixture containing oxygen, Hermann found that he could establish no physiological absorption of that gas; a small amount of it disappeared, and there was a small increase in the quantity of carbonic anhydride evolved, but both these phenomena were dependent on decomposition going on at the surface of the muscle, and were proportional to its area and not to the work done; the irritability of the muscle, however, was somewhat longer preserved in gaseous mixtures containing oxygen than in others; and this may be attributed either to a very small and otherwise unrecognisable physiological assumption of oxygen, or perhaps to some specific action of the oxygen, promoting the excretion of the carbonic anhydride formed in the muscle.

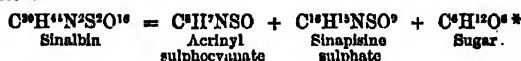
If we now consider the relationship of contraction and *rigor mortis*, we find that, so far as the carbonic anhydride and lactic acid are concerned, the chemistry of the two processes is identical, and that they are also quantitatively related; for, as above stated, if a muscle be thrown into a state of *rigor* after having been made to contract, the quantity of carbonic anhydride which it evolves is less than that which an unworked muscle would have evolved, by exactly the amount which was evolved during its contraction; we have apparently, however, a difference between the two processes in the stiffening of *rigor mortis*. Du Bois Reymond and Kuhne maintain that the acidity of tetanised muscle differs from that of stiffened muscle in the fact that the former can be removed by restoring the circulation through the muscle, and the latter not. Hermann, however, shows that this difference is really only one of degree, for if a muscle be rendered acid by commencing *rigor* (induced by heat), while the blood current is not interrupted in it, this acidity can be removed by the blood flow; in other words, if the *rigor mortis* is not allowed to go too far, the state of the muscle as regards the acidity is the same both in tetanus and in death-stiffening. Du Bois Reymond also points out that if a muscle be tetanised till it will no longer contract, and be then left to itself for a time, it will again become contractile; and he maintains that such restoration never occurs after *rigor mortis*; this statement, however, is also true only of advanced, not of incipient *rigor*. Fresh muscle-plasma sets, soon after extraction, into a clear semi-solid jelly (myosin), which after a time separates into a completely fluid portion and a dense clot (coagulated myosin), the latter at the same time becoming opaque. It is evidently this second stage of the myosin coagulation which corresponds with the condition of things in a completely stiffened and opaque muscle; but it must be preceded by the former, in which the setting of the myosin is not sufficiently firm to make any rigidity recognisable, and when as yet no opacity has been developed. This early stage of *rigor mortis*, which can only be recognised by the development of an acid reaction in the muscle, and the concomitant evolution of carbonic anhydride, is evidently the stage which should be compared with the state of a muscle exhausted by tetanus. The non-coagulated jelly-like myosin of this early stage of *rigor* can be restored to its original state by the blood, the muscle at the same time losing its acidity and returning in every respect to its normal state. If, however, the myosin has coagulated and become opaque, the blood is unable alone to restore the muscle; but, as Preyer (*Centr. f. d. Med. Wiss.* 1864, s. 769-773) has shown, if the coagulated myosin be dissolved by soaking the muscle in a 10 p.c. solution of sodium chloride, then restitution by the blood is possible. Coagulated myosin must then present an obstacle to the restoration of the muscle, which myosin before it has coagulated does not present.

The conclusion which Hermann arrives at is therefore as follows: That muscular work, though in the long run dependent on oxidation, is not immediately so; but that a living muscle contains a store of some substance (*inogen*) which, when the muscle contracts, breaks up in proportion to the work done (and independently of any taking up of oxygen) into carbonic anhydride, lactic acid, myosin, and possibly some other bodies. In these products of decomposition stronger affinities are satisfied than in the original compound, and thus energy is set free and manifests itself as muscular work. The substances which the muscle loses during contraction (and which are normally carried off by the blood) contain no nitrogen: for the myosin remains in the muscle in its jelly-like form, and is used again, being built up, by the aid of oxygen and non-nitrogenised compounds conveyed to it by the blood, into the original unstable muscle com-

pound, which is again stored away ready for use. If, however, the muscle be removed from the blood-current, or be heated to 50° C., the jelly-like myosin first separated soon passes into its firmly coagulated stage, and is then unfit for further use in the muscle; possibly a small amount of this may be formed in an overworked muscle, and be afterwards broken up and carried away in the form of simpler compounds; but if any great amount of it is formed, then the blood cannot restore the muscle, which remains (until decomposition sets in) in a state of *rigor mortis*. The energy set free during the formation of the carbonic anhydride, &c., and showing itself normally as a muscular contraction, must, of course, in a muscle passing into the state of death-stiffening, take some other form, and probably appears as heat. Whether the lactic acid formed in a contracting muscle is carried away, or is used again like the myosin, is uncertain.

H. N. M.

**MUSTARD.** White mustard seed contains a glucoside, sinalbin, which is soluble in alcohol, and, like potassium myronate, decomposes in contact with aqueous extract of mustard:—



an albuminous substance being likewise formed. Acrylyl sulphocyanate resembles oil of mustard, is soluble in ether, very pungent, insoluble in water, but not volatile; after warming with an alkali and neutralisation with an acid, it gives a red colour with ferric chloride. Sinapisine sulphate is insoluble in ether.

Sinalbin gives a white precipitate with silver nitrate, from which sulphydric acid removes the silver, leaving acrylyl cyanate,  $\text{C}^6\text{H}^7\text{NO}$ , fusible at 60°, easily soluble in water, alcohol, and ether. When boiled with potash it gives ammoniac and the potassium salt of an acid,  $\text{C}^6\text{H}^7\text{O}^3$ , fusible at 136°, but apparently different from the known acid of this composition (Will, *Zeitschr. f. Chem.* [2], vii. 89).

The relations of these compounds to the other constituents of mustard do not appear to have been made out.

On Volatile Oil of Mustard, see SULPHOCYANATES.

**MYCOMELIC ACID**,  $\text{C}^6\text{H}^7\text{N}^4\text{O}^2$ . This compound, which Liebig & Wöhler obtained by the action of ammonia on alloxan (iii. 1068), is likewise produced by the action of boiling water on azulmic acid or hydrazalmozin (p. 416).

**MYELIN.** The lithomarge from Rochlitz in Saxony, known as myelin, has been variously represented by the formulæ  $\text{Al}^2\text{O}^3 \cdot \text{SiO}^2$  (Kersten) and  $2\text{Al}^2\text{O}^3 \cdot \text{SiO}^2 + \text{H}^2\text{O}$  (Breithaupt). To ascertain its true composition, Frenzel (*J. pr. Chem.* [2], v. 401) analysed a pure snow-white kidney-shaped specimen carefully freed from adhering ferric oxide. This mineral gave, in two analyses, the following results:—

	$\text{SiO}^2$	$\text{Al}^2\text{O}^3$	$\text{CaO}$	$\text{H}^2\text{O}$
a. . . . .	43.94	39.40	0.42	17.11 = 100.87
b. . . . .	44.19	39.68	0.47	16.67 = 100.81

The pulverised mineral heated to 100° gives off 2.56 and 2.30 p.c. hygroscopic water. On deducting this water and the lime, the preceding analyses gave:—

	$\text{SiO}^2$	$\text{Al}^2\text{O}^3$	$\text{H}^2\text{O}$
a. . . . .	45.27	40.59	14.55
b. . . . .	45.44	40.60	14.27

leading to the formula  $\text{Al}^2\text{O}^3 \cdot 2\text{SiO}^2 + 2\text{H}^2\text{O}$ , which agrees with that of nacrite, kaolin, carnat, and the lithomarge of Schenckenstein near Auerbach, Cainsdorf near Zwickau, and a few other localities. All these minerals give up more or less hygroscopic water at 100°, namely: carnat from Rochlitz, 1.8; lithomarge from Auerbach, 1.2; nacrite from Freiberg, 0.8; and kaolin from Seilitz, 0.15 p.c.

Myelin appears homogeneous under the microscope, and does not polarise light, in which respect it resembles carnat. Nacrite, on the other hand, crystallises in hexagonal plates; kaolin and lithomarge from the above-mentioned localities are likewise crystalline. The crystalline characters of nacrite, kaolin, and crystalline lithomarge, are not sufficiently well made out to enable us to decide whether these minerals belong to one and the same species. Kennigott proposed to unite nacrite with kaolin; crystalline lithomarge is regarded as a hardened kaolin. On the other hand, the amorphous varieties of lithomarge, namely myelin and carnat, are identical, and it would therefore be advisable to discard the name carnat altogether.

Myelin of the same composition as that found by Kersten is said to occur at Ziboraz near Temesvar in Hungary.

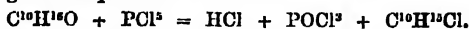
**MYRISTICENE**,  $\text{C}^{14}\text{H}^{28}$ . The terpene obtained from nutmeg.

\* There is an error in this equation: either sinalbin must contain  $\text{H}^2$ , or sinapisine must contain  $\text{H}^2$ .

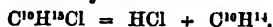


**MYRISTICOL.** An oxidised oil forming the chief constituent of the volatile oil of nutmeg, from which it may be separated by fractional distillation. It was first obtained by Gladstone (*Chem. Soc. J.* [2], x. 11), and has been further examined by Wright (*ibid.* xi. 549, 686). It has the characteristic smell of nutmeg; boils at about 220° (Gladstone) or between 212° and 218° (Wright); has a high refractive power (p. 739). Gladstone obtained by its analysis numbers agreeing approximately with the formula  $C^{10}H^{16}O$ . Wright, on the other hand, regards it as isomeric with ordinary camphor,  $C^{10}H^{16}O$ , his analysis giving 78.8 and 78.3 p.c. carbon and 10.3 hydrogen, and the formula  $C^{10}H^{16}O$  requiring 78.94 C. and 10.53 H., whereas  $C^{10}H^{16}O$  requires 80.00 C. and 9.33 H.

Myristicol, treated with phosphorus pentachloride, is decomposed in the manner of alcohols, according to the equation:



The chlorinated compound thus obtained is crystalline, and melts at 100°. When heated for some time, or repeatedly distilled at a very slow rate, it splits up in the manner of secondary alcohols, yielding hydrogen chloride and a hydrocarbon containing the elements of water less than myristicol:



The hydrocarbon thus obtained is ordinary cymene (p. 419).

**MYRTENE**,  $C^{10}H^{14}$ . The terpene from volatile oil of myrtle.

## N

**NADORITE.** This name is given by Flajolot (*Compt. rend.* lxxi. 237) to a lead-ore from a vein of galena near the hot spring of Hamman-Nbail-Nador, in the province of Constantine, Algeria, to which he originally assigned the formula  $Sb^{20}O^4.PbO$ , deduced from an analysis which gave 44 p.c.  $Sb^{20}O^4$ , and 56 PbO. Pisani, on the other hand (*ibid.* 319), finds that the mineral contains chlorine as an essential constituent, and gives by analysis numbers agreeing with the formula  $Sb^{20}O^4.PbCl^2$ —

	$Sb^{20}O^4$	PbO	Pb	Cl	
Analysis	37.40	27.60	26.27	9.00	= 100.27
Calculation	36.82	28.12	26.11	8.95	= 100

Flajolot (*ibid.* 406), on repeating his analysis, found 51.60 p.c. Pb, 32.25 Sb, 8.00 O, and 8.85 Cl, whence he deduces the formula  $SbOCl.PbO$ , agreeing in percentage composition with that of Pisani.

In an oxidation-product of nadorite Flajolot found—

$Sb^{20}O^4$	$Sb^{20}O^4$	$CO^2$	PbO	$H^2O$
4.80	35.50	4.20	51.50	4.00

and supposing the antimonious oxide to be an incompletely oxidised residue of the original substance, he regards the mineral as a definite compound, represented by the formula  $PbO.Sb^{20}O^4 + PbO.CO^2 + 2H^2O$ . Pisani, on the contrary, regards it as a mixture of bleinorite (i. 326) and cerussite, crystals of the latter of which are indeed implanted on it.

Lastly, Flajolot regards an amorphous argillaceous mass from the same locality, containing 63.50 p.c.  $Sb^{20}O^4$ , 31.40  $Fe^{20}O^3$  and 5.10  $H^2O$ , likewise as a distinct mineral species, represented by the formula  $2(Fe^{20}O^3.Sb^{20}O^4).3H^2O$ .

**NAPHELINE.** See ACONITE ALKALOIDS (p. 23).

**NAPHTHALENE**,  $C^{10}H^8$ . *Synthesis.*—This hydrocarbon is formed by passing the vapour of phenylbutylene bromide,  $C^{10}H^{12}Br^2$ , over quicklime heated to dull redness—



The phenylbutylene (*q. v.*) is obtained by treating an ethereal solution of benzyl bromide and allyl iodide with sodium, distilling, and collecting the portion which passes over between 176° and 178°. The decomposition of its bromide yields nearly the theoretical quantity of naphthalene (Aronheim, *Deut. Chem. Ges. Ber.* vi. 67).

*Properties.*—According to Ballé, perfectly pure naphthalene has merely a faint and

by no means unpleasant odour, the pungent odour of (so-called) pure commercial naphthalene being due to admixed leucoline oil, which may be separated from it by boiling with strong sulphuric acid, and precipitating the resulting brown solutions with ammonia (p. 787).

**Reactions.**—Naphthalene exposed to the vapour of *nitromuriatic acid* at ordinary temperatures, is converted into naphthalene tetrachloride,  $C^{10}H^4Cl^4$ , and chloronaphthalene tetrachloride,  $C^{10}H^3Cl^4$  (Bunge, *Deut. Chem. Ges. Ber.* iv. 289). It is not acted upon by phosgene (Berthelot, *Bull. Soc. Chim.* [2], xiii. 301). For its reaction with *sulphuryl hydroxychloride*,  $SO^2HCl$ , see NAPHTHALENE-SULPHONIC ACID (p. 835).

#### Compounds and Derivatives of Naphthalene.

**Acenaphthene**,  $C^{12}H^{10}$ . This hydrocarbon, which occurs in heavy coal-tar oil, and is formed synthetically by passing a mixture of naphthalene-vapour and ethylene through a red-hot tube (1st *Suppl.* p. 3), may also be produced from ethyl-naphthalene (*ibid.* 849) by passing the vapour of that compound through a porcelain tube at a bright red heat, whereby naphthalene and acenaphthene are produced, and may be separated by fractional distillation. The change may be also effected in the wet way by heating ethylene-naphthalene to  $180^\circ$  with two equivalents of bromine, treating the crude liquid (which cannot be purified by distillation) with alcoholic potash at  $100^\circ$ , and at the end of twelve hours pouring the mother-liquor into water. The heavy oily layer which separates is distilled, and the portion passing over at  $300^\circ$  is treated with alcoholic picric acid. The red precipitate, decomposed by ammonia, gives a liquid which deposits crystals of acenaphthene (Berthelot a. Bardy, *Compt. rend.* lxxiv.). According to Graebe (*Deut. Chem. Ges. Ber.* v. 15), acenaphthene melts at  $99^\circ$ – $100^\circ$ , and has a vapour-density of 5.35 (calc. 5.33). According to Behr and van Dorp (*ibid.* vi. 60) it melts at  $94^\circ$ – $96^\circ$ , distils at  $267^\circ$ – $269^\circ$  (uncorrected), and is oxidised by boiling with chromic acid mixture to naphthophthalic acid,  $C^{10}H^4(CO^2H)^2$ .

On Naphthalene Tetrachloride and the Chloronaphthalenes, see 1st *Suppl.* 846–847.

According to Grimaux (*Bull. Soc. Chim.* [2], xviii. 205) the tetrachloride heated with 30 parts of water to  $180^\circ$ – $190^\circ$  for some hours, or boiled with water, is converted into dichloronaphthhydrenglycol,  $C^{10}H^2Cl^2(OH)^2$ .

**Nitronaphthalenes** (A. de Aguiar, *Deut. Chem. Ges. Ber.* v. 370). Compare iv. 14 and 1st *Suppl.* p. 848. At least seven distinct nitro-compounds are producible by the action of nitric acid on naphthalene, and may be separated with more or less difficulty by fractional crystallisation, glacial acetic acid serving better as a solvent than ethyl or methyl alcohol, benzene, or chloroform.

**Mononitronaphthalene** is best prepared by treating naphthalene dissolved in boiling glacial acid, with ordinary nitric acid, and boiling for half an hour. No red vapours are evolved, and on cooling, the whole becomes a mass of crystals, which are perfectly pure after one crystallisation from alcohol. According to De Aguiar, the pure compound melts at  $61^\circ$ , which is some degrees higher than the melting point found by Laurent, viz.  $43^\circ$ .

**Dinitronaphthalene.**—Fuming nitric acid and naphthalene, boiled together for some hours, yield this compound in two modifications,  $\alpha$  and  $\beta$ , in nearly equal quantities. On cooling, a crystalline mass separates, usually containing only traces of trinitronaphthalene. This mass is washed and dried, and then boiled with glacial acetic acid (about 2½ times its weight). Pure  $\alpha$ -dinitronaphthalene remains undissolved, and may be crystallised from a large quantity of fresh acid. The  $\beta$  modification is much more soluble than the  $\alpha$ , and is readily obtained pure by a few fractional crystallisations of the product obtained from the dissolved part. The two bodies differ in their crystalline forms and melting points, the  $\alpha$  modification melting at  $216^\circ$  and the  $\beta$  at  $170^\circ$ . A small quantity of what appears to be a third modification is also obtained, but cannot readily be purified, as its solubility is nearly the same as that of  $\beta$ -dinitronaphthalene.

**Trinitronaphthalene.**—Two modifications of this derivative exist, and may be obtained by the action of nitric acid on naphthalene; their separation and purification are however difficult. Much better results are obtained by nitrating  $\alpha$ - and  $\beta$ -dinitronaphthalene in sealed tubes at  $120^\circ$ – $130^\circ$ , or in a retort with inverted condenser.  $\alpha$ -dinitronaphthalene, thus treated, gives a product which after precipitation by water and crystallisation from alcohol, benzene, glacial acetic acid, or chloroform (the last being the best), yields fine crystals of  $\alpha$ -trinitronaphthalene, melting at  $128^\circ$  and solidifying at  $90^\circ$ .  $\beta$ -dinitronaphthalene yields in like manner  $\beta$ -trinitronaphthalene melting at  $218^\circ$ ; the latter is much less soluble in alcohol and chloroform than the former, but may be crystallised from these solvents.

Beilstein a. Kuhlberg (*Deut. Chem. Ges. Ber.* v. 480), by treating dinitronaphthalene (m.p.  $212^{\circ}$ ) with a mixture of nitric and sulphuric acids, have likewise obtained two trinitronaphthalenes, one probably identical with Laurent's, melting at  $208^{\circ}$ , the other at  $147^{\circ}$ .

*Tetranitronaphthalene*.—If the action of the nitric acid in preparing trinitronaphthalene be carried on for two days, tetranitrated bodies are formed.  $\alpha$ -tetranitronaphthalene obtained from  $\alpha$ -dinitronaphthalene is almost insoluble in alcohol, cannot be crystallised from acetic acid, but crystallises readily from chloroform, the crystals melting at  $259^{\circ}$  and solidifying at  $225^{\circ}$ .  $\beta$ -tetranitronaphthalene melts at  $200^{\circ}$  (De Aguiar).

**NAPHTHALENE COLOURS** (Ballò, *Dingl. pol. J.* xciv. 82). A mixture of fuchsine and monobromonaphthalene forms when heated a violet colouring matter similar in every respect to Hofmann's violet. The saturated alcoholic solution of this dye-stuff has a deep violet colour almost black; in the solid state the substance resembles fuchsine. On adding a small quantity of hydrochloric acid, the colour of the alcoholic solution changes to blue and on further addition to green. The addition of an alkali, or even of alcohol, brings about the same changes of colour in the reverse order.

**NAPHTHALENE-CARBOXYLIC ACID.** Syn. with NAPHTHOIC ACID.

**NAPHTHALENE-POTASSIUM**,  $C^{10}H^8K^2$ . The substance formed by fusing naphthalene with potassium (*1st Suppl.* 844) is converted by heating with ethyl bromide into a hydrocarbon,  $C^{20}H^{12}$  (? dinaphthyl) (Abeljan, *Deut. Chem. Ges. Ber.* v. 102).

**NAPHTHALENE-SULPHONIC ACID.** According to Merz a. Weith (*Deut. Chem. Ges. Ber.* iii. 195), the action of sulphuric acid upon naphthalene at comparatively high temperatures ( $160^{\circ}$ – $170^{\circ}$ ) yields chiefly the  $\beta$  modification of naphthalene-monosulphonic acid,  $C^{10}H^7SO^3H$ , whereas at lower temperatures ( $80^{\circ}$ – $100^{\circ}$ ) the product consists chiefly of the  $\alpha$  modification (*1st Suppl.* 860). In mixtures containing a considerable proportion of the  $\alpha$ -acid, the separation of the two is best effected by converting them into calcium salts, the  $\alpha$ -salt being the more soluble of the two. The  $\alpha$ -sulphonic acid is partially converted into the  $\beta$  modification when its lead salt is heated to  $100^{\circ}$  with moderately concentrated sulphuric acid.

By treating naphthalene with *sulphuryl hydrozylchloride*,  $SO^2.OH.Cl$ , both modifications of the monosulphonic acid appear to be produced. With 2 mol. of the hydrozylchloride to 1 mol. naphthalene, the disulphonic acid,  $C^{10}H^6(SO^3H)^2$ , is obtained (Armstrong, *Chem. Soc. J.* [2], ix. 173).

**NAPHTHAQUINONE**,  $C^{10}H^6O^2$ . This compound, which Hermann obtained in small quantity by the dry distillation of potassium chloronaphthasulphoquinonate (*1st Suppl.* 852), has lately been obtained more abundantly and in greater purity by C. E. Groves (*Chem. Soc. J.* [2], xi. 209) by the application of Graebe a. Liebermann's method of preparing quinones—namely, by oxidising naphthalene with a solution of chromic anhydride in glacial acetic acid. For this purpose a solution of naphthalene in warm glacial acetic acid was treated with an almost saturated solution of chromic anhydride in the same solvent, whereby great heat was evolved, the solution turning green and depositing a green chromium salt on the sides of the vessel. As soon as the reaction was complete, the product was diluted with water, which dissolved the chromium salt, and at the same time produced an orange-coloured precipitate containing the impure naphthaquinone. This, when collected, washed, and dried, was of a deep-yellow colour, and had a strong odour, arising from the naphthalene which had escaped the action of the chromic anhydride. As the naphthaquinone in this precipitate was accompanied by a certain amount of black tarry matter, very difficult to separate by crystallisation, it was found advantageous to purify it partially by distillation in the vapour of water, in which it volatilises easily, although not so readily as naphthalene. The long, bright-yellow crystals which adhered to the sides of the condensing tube, consisting almost entirely of naphthaquinone and naphthalene, were either at once purified from the latter by alternate crystallisation from light petroleum oil, carbon bisulphide, and alcohol; or the greater part of the naphthalene was previously removed by allowing the mixture to remain freely exposed to the air for some time in a warm place.

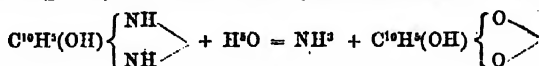
Naphthaquinone identical with the above is produced by oxidising the hydrochloride of amidacetonaphthalide,  $C^{10}H^8\{NH(CO.CH^3)\}_2$ , with a 1 p.c. solution of chromic acid ( $NH^2.HCl$ ) (Liebermann a. Dittler, *Deut. Chem. Ges. Ber.* vi. 945).

Naphthaquinone, prepared by either of these processes, is a bright-yellow crystalline substance, which melts at about 125°, and begins to sublime below 100°. Although but slightly soluble in cold water, it is readily volatile in vapour of water at 100°, communicating to it a pungent odour, like that which is so characteristic of ordinary quinone. It is but slightly soluble in light petroleum oil, readily in benzene, carbon bisulphide, chloroform, and other, especially when hot, and crystallises by spontaneous evaporation from its solution in the latter in well-formed rhomboidal plates. It is very soluble in boiling alcohol, but crystallises out in great part on cooling. It dissolves in concentrated sulphuric acid, and in glacial acetic acid, being again precipitated on the addition of water; also in alkalis, forming a reddish-brown solution, in which acids cause a precipitate of a bright-red colour, the nature of which has not yet been examined. When the quinone is boiled with concentrated hydrochloric acid, it is apparently converted into hydromonochloronaphthaquinone in a manner similar to that in which hydrochloroquinone is formed from ordinary quinone (Groves). When boiled with pure nitric acid, it is oxidised to phthalic acid (Liebermann a. Dittler).

*Hydronaphthaquinone*,  $C^{10}H^8O = C^{10}H^7(OH)^2$ .—A cold aqueous solution of sulphurous anhydride is almost without action on naphthaquinone, but when the latter is boiled with strong hydriodic acid and amorphous phosphorus, it dissolves, forming a colourless solution which deposits long needles of the hydronaphthaquinone on cooling. This compound crystallises in colourless needles which melt at about 176° and dissolve with comparative readiness in boiling water, crystallising out again, in great part, on cooling. It is readily soluble in alcohol and ether, even in the cold, also in glacial acetic acid, slightly soluble in hot benzene, crystallising out again on cooling in tufts of colourless needles, and almost insoluble in carbon bisulphide and light petroleum oil. When treated with oxidising agents, such as chromic acid, &c., it is reconverted into the quinone.

On boiling an aqueous solution containing a molecular weight of hydronaphthaquinone with a molecular weight of naphthaquinone, the latter dissolved, yielding a pale-brown solution which, as it cooled, deposited the dark-purple crystalline naphthaquinhydrone,  $C^{20}H^{14}O^4$ , analogous to the quinhydrone or green hydroquinone of the benzene series. The same purple quinhydrone was obtained when naphthaquinone was boiled with amorphous phosphorus and a weak solution of hydriodic acid. It is readily converted, by treatment with strong hydriodic acid, into colourless hydronaphthaquinone on the one hand, and by oxidising agents into naphthaquinone on the other (Groves).

**Oxynaphthaquinones.** *Monooxynaphthaquinone* or *Naphthalic acid*,  $C^{10}H^6O^3 = C^{10}H^4(OH)\begin{Bmatrix} O \\ O \end{Bmatrix}$ , is most easily formed by heating the hydrochloride of di-imidonaphthol (p. 841) to 120° with *dilute* hydrochloric or sulphuric acid:



It dissolves sparingly in water, easily in alcohol and in ether. Reducing agents convert it into dioxynaphthol; zinc-dust, with the aid of heat, into naphthalene. It exhibits the characters of a strong acid. Its *ammonium salt* is a red, crystalline, easily soluble mass. The *silver salt* crystallises in cinnabar-red needles. The *ammonium salt* forms with ferric chloride a red-brown precipitate, with cupric sulphate a brownish red, with mercury salts an orange-coloured, and with barium chloride a red precipitate (Graebe a. Ludwig, *Ann. Ch. Pharm.* cliv. 303).

*Dioxynaphthaquinone* or *Naphtazarin*,  $C^{10}H^4O^4 = C^{10}H^2(OH)^2\begin{Bmatrix} O \\ O \end{Bmatrix}$

This substance was first obtained by Roussin (iv. 18) by the action of strong sulphuric acid and zinc on dinitronaphthalene. It sublimes in small red-brown crystals, or in long needles having a bright green metallic lustre. With baryta- and lime-water it gives fine violet-blue precipitates; with magnesia, a crimson; with basic lead acetate, a blue; and with ferric salts a black precipitate. Ammonia dissolves naphtazarin with a sky-blue colour, which by long standing changes to a reddish-violet; concentrated sulphuric acid gives in the cold a beautiful magenta-coloured solution from which water precipitates red flocks. It dissolves slowly in boiling water, more easily in alcohol, and crystallises therefrom. By heating with zinc-dust it is reduced to naphthalene (Liebermann, *Deut. Chem. Ges. Ber.* iii. 706).

De Aguiar a. Baeyer (*ibid.* iv. 251, 438) find that naphtazarin is formed from the modification of dinitronaphthane (melting at 214°). To prepare it, the dinitronaph-

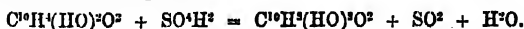
lene was added to sulphuric acid heated to  $200^{\circ}$ , and then zinc in small portions; the temperature was kept constant for about twenty minutes, and then the mixture was allowed to cool; when cold it was treated with boiling water and left at rest for 48 hours. The precipitate was then filtered off, slightly washed with cold water, and treated with strong aqueous potash, any traces of unaltered dinitronaphthalene being removed by filtration. The beautifully coloured blue liquid was now supersaturated with dilute sulphuric acid, whereby the crude naphthazarin was slowly precipitated; it was then filtered off and dried at  $100^{\circ}$ . As thus prepared it contains a black substance, which cannot be separated by sublimation, as a large portion of the naphthazarin becomes carbonised at the same time. The purification may, however, be effected by dissolving the crude naphthazarin in warm glacial acetic acid, filtering from the undissolved black substance, and distilling at a temperature a little above  $130^{\circ}$ . The naphthazarin is thereby obtained as a crystalline substance having a metallic lustre.

The same result is obtained by heating  $\alpha$ -dinitronaphthalene with sulphuric acid without the aid of zinc. In this case it is not necessary, as stated by Persoz (*Compt. rend.* lii. 1178), to raise the temperature above  $200^{\circ}$ , but the heating must be continued three times as long as when zinc is employed. When 4 grams of dinitronaphthalene were heated with sulphuric acid to  $200^{\circ}$  till the whole was converted into naphthazarin, 450 c.c. of gas were obtained, containing in 100 volumes  $86\cdot15$  vol.  $\text{SO}_2$ , 701 N., and  $6\cdot54$   $\text{CO}_2$ .

In the blue liquid above mentioned, from which naphthazarin separates on boiling, the formation of that substance likewise goes on in the cold, inasmuch as the blue colour gradually changes to red. Nevertheless, the blue solution does not contain naphthazarin ready formed, and it contains only a small portion of ammonia, the quantity of which is, however, considerably increased by boiling. If the sulphuric acid be removed by barium carbonate, a bluish-violet liquid is obtained, which, after removal of the carbonate, still contains barium. It turns blue when acidulated, and red when heated, ammonia being then formed and naphthazarin becoming recognisable. From the acidulated liquid containing barium, and likewise from the original blue-violet liquid, there is deposited, on standing, a second compound distinguished from naphthazarin both by the violet colour of its solutions and by its different chemical behaviour. This body likewise yields naphthazarin, with separation of ammonia, but the transformation is somewhat slower than that which takes place in the solution. This last-mentioned compound is usually present in naphthazarin prepared by Roussin's process. The greater part of it carbonises when heated (De Aguiar a. Bayer).

*Trioxynaphthaquinone*,  $\text{C}^{10}\text{H}^6\text{O}^3 = \text{C}^8\text{H}^4(\text{OH})^2 \left\{ \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \right.$  This is the

chief constituent of the black substance above mentioned. To prepare it the cooled product of the action of sulphuric acid on dinitronaphthalene is mixed with water, and the black precipitate filtered off from the blue-violet solution is repeatedly boiled with water acidulated with sulphuric acid; much ammonia then passes into solution. The product is dissolved in soda-solution, again precipitated by sulphuric acid, the precipitate well washed with hot water, and then dried at  $100^{\circ}$ . The product thus purified has the composition of trioxynaphthaquinone. The same body is obtained by the action of sulphuric acid on pure naphthazarin, its formation, in this case, being possibly in accordance with the equation:



Thus prepared it is amorphous with a reddish metallic gloss, cannot be sublimed, dissolves in alkalis with a dirty blue-violet colour, and tinges hot water pale-red. On reduction with zinc-dust it yields naphthalene.

In an operation in which the heating had been carried too far, a body was obtained which, after purification in the same manner, gave on analysis less C and H than the above, and appeared to consist of a mixture of tri- and tetra-oxynaphthaquinone (De Aguiar a. Bayer).

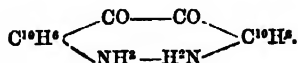
**NAPHTHOIC ACID**,  $\text{C}^{10}\text{H}^8\text{O}^3 = \text{C}^{10}\text{H}^7\text{COOH}$ . Respecting the formation, properties, reactions, and salts of this acid, see 1st Suppl. p. 861.

$\alpha$ -Naphthoic acid, oxidised with potassium permanganate, is converted into an acid which, after purification, crystallises in slender needles, yields an easily soluble potassium salt, and flocculent, nearly insoluble lead and barium salts (Carstanjen a. Schertel, *J. pr. Chem.* [2], iv. 49).

*Nitronaphthoic acids*.— $\alpha$ -Mononitronaphthoic acid,  $\text{C}^{10}\text{H}^7(\text{NO}^2)\text{O}^2$ , is prepared by adding a mixture of  $\alpha$ -naphthoic acid and potassium nitrate to sulphuric acid, and heating over the water-bath. When purified by sublimation it forms shining radiate

tufts of slender needles, having a faint yellowish colour; melts at  $194^{\circ}$ .  $\beta$ -Nitronaphthoic acid is prepared in like manner from  $\beta$ -naphthoic acid, the mixture being, however, finally heated over the open fire to complete the action. It resembles the  $\alpha$ -acid, but melts at  $288^{\circ}$ . Both these nitro-acids dissolve sparingly in water, more freely in alcohol. Their alkali-salts have a yellow to orange-yellow colour; the barium and silver salts are faintly yellowish flocculent precipitates, slightly soluble in cold, more soluble in hot water. The lead and copper salts are precipitates only sparingly soluble even in hot water (O. Küchenmeister, *Deut. Chem. Ges. Ber.* iii. 739).

When  $\beta$ -nitronaphthoic acid is treated with tin and hydrochloric acid, a violent action takes place, and on boiling the product with ammonium carbonate and filtering, the liquid, on cooling, deposits a substance which, when recrystallised from weak alcohol, has the composition  $C^{11}H^6NO$  or  $C^{22}H^{16}N^2O^2$ , and probably the constitutional formula:



The same compound is obtained by the action of iron and acetic acid on  $\beta$ -nitronaphthoic acid.

This substance does not combine either with acids or with bases, and is not precipitated from its solution in hot water by the addition of metallic salts. It is scarcely soluble in cold water, but more soluble in that liquid when hot, and is deposited, on cooling, in microscopic flexible needles. Ether and alcohol dissolve it readily, and the latter deposits it in tolerably long prisms. It melts at  $174^{\circ}$ , solidifies at  $165^{\circ}$ , and begins to sublime in small needles at  $125^{\circ}$ . Concentrated sulphuric acid dissolves it, and it is precipitated from the solution on the addition of water. When potassium bichromate is added to its solution in sulphuric acid, the liquid becomes dark blue, and the addition of water causes the separation of violet flocks.

$\beta$ -Nitronaphthoic acid, treated with ammonium sulphide, yields, not amidonaphthoic acid, but a small quantity of azonaphthoic acid,  $CO^2H - C^6H^4 - N = N - C^6H^4 - CO^2H$  (P. v. Rakowski, *Deut. Chem. Ges. Ber.* v. 1020).

**Oxynaphthoic Acids**,  $C^{11}H^6O^2 = C^6H^4(OH.CO^2OH)$ .—These acids are produced by fusing the potassium salts of the corresponding sulphonaphthoates with potassium hydrate. The  $\alpha$ -acid dissolves freely in alcohol and with moderate facility in boiling water, and crystallises from a hot aqueous solution in long interlaced needles, melting at  $234^{\circ}$ – $237^{\circ}$ , and subliming, when carefully heated, in feathery crystals. On boiling down the aqueous solutions of its salts, the liquid darkens and a dark amorphous mass separates out.

The  $\beta$ -acid crystallises from boiling water in long needles, melting at  $212^{\circ}$ – $213^{\circ}$ . Its salts are as unstable as the  $\alpha$ -oxynaphthoates (J. P. Battershall, *Ann. Ch. Pharm.* clxviii. 114).

**Sulphonaphthoic Acids**,  $C^{11}H^6SO^3 = C^6H^4 \begin{cases} CO.OH \\ SO^2OH \end{cases}$  (Battershall. *loc. cit.*; also *Zeitschr. f. Chem.* [2], vii. 673).—Fuming sulphuric acid converts naphthoic acid into a mixture of at least two sulpho-acids, both of which yield crystallisable barium salts,  $C^6H^4(SO^2)(CO^2)Ba$ . On neutralising the mixture of the sulpho-acids with barium carbonate, the  $\alpha$ -salt crystallises out first, and this when decomposed by sulphuric acid yields  $\alpha$ -sulphonaphthoic acid. This acid dissolves readily in water and crystallises therefrom in colourless needles, melting with slight decomposition at  $230^{\circ}$ – $240^{\circ}$ .

Its barium salt,  $C^6H^4(SO^2)(CO^2)Ba + 4H^2O$ , forms well-defined, glistening, transparent, and compact monoclinic crystals. The calcium salt,  $C^6H^4(SO^2)CO^2Ca + 3H^2O$ , is moderately soluble in water, and crystallises in thin plates. The potassium salt,  $C^6H^4(SO^2K)(CO^2K) + 2H^2O$ , forms thin tables and is freely soluble in water. The cupric salt,  $C^6H^4(SO^2)(CO^2)Cu$ , is a bluish-green precipitate, sparingly soluble in boiling water.

$\beta$ -Sulphonaphthoic acid is produced by dissolving  $\beta$ -naphthoic acid in fuming sulphuric acid. It forms a very characteristic acid barium salt,  $(C^{11}H^4SO^2)Ba + 7H^2O$ , which is almost insoluble in cold water, and crystallises from a boiling solution in brilliant large plates. The neutral salt,  $C^{11}H^4SO^2Ba + H^2O$ , is readily soluble in water, and forms oblique crystals.

**NAPHTHOIC ALDEHYDE**,  $C^{11}H^6O$  (Battershall, *Zeitschr. f. Chem.* [2], vii. 292, 673).  $\beta$ -Naphthoic aldehyde is produced by distilling an intimate mixture of calcium naphthoate and calcium formate at a high temperature. The distillate contains naphthalene together with the aldehyde, which may be purified by shaking it with

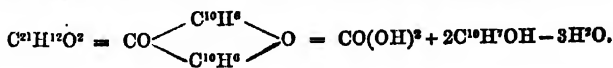
sodium bisulphite, washing the resulting crystalline mass with ether till it becomes colourless, and distilling the crystals with dilute solution of sodium carbonate. The aldehyde then passes over with the vapour of water, and solidifies in the condensing tube in dazzling white crystals. It is very nearly insoluble in cold water, somewhat soluble in boiling water, very soluble in alcohol and ether. It crystallises from boiling water in very bulky, thin, shining laminae, and is obtained in the same form by spontaneous evaporation of its alcoholic solution. It melts at  $59^{\circ}5'$ . Potassium permanganate oxidises it readily when heated with it, forming potassium  $\beta$ -naphthoate, with separation of hydrated manganic oxide. Strong nitric acid dissolves it at a gentle heat, forming a crystalline non-acid compound which separates on the surface of the liquid. Nascent hydrogen converts it into uncrystallisable compounds difficult to purify. It dissolves easily in alcoholic ammonia, and is thereby converted into  $\beta$ -hydronaphthamide.

*$\alpha$ -Naphthoic aldehyde.*—A mixture of calcium formate and pure calcium  $\alpha$ -naphthoate yields by distillation scarcely anything but naphthalene, only the merest traces of the aldehyde being formed, if any. The cause of this negative result is doubtless that calcium  $\alpha$ -naphthoate is resolved into naphthalene and calcium carbonate at a temperature lower than that which is required to bring about its reaction with the formate. When, however, a mixture  $\alpha$ -naphthoate containing  $\beta$ -naphthoate is used, a distillate is obtained which, when purified as above with sodium bisulphite, yields liquid  $\alpha$ -naphthoic acid containing a certain portion of the  $\beta$  compound, which after a while separates in crystals.

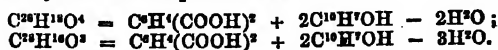
$\alpha$ -Naphthoic aldehyde is a somewhat thick liquid having a peculiar faint smell, and becoming coloured on exposure to the air. It is heavier than water, boils at about  $280^{\circ}$ , but cannot be distilled without forming a small quantity of condensation-products of higher boiling point; with steam, however, it volatilises readily and without alteration.

**NAPHTHOLS**,  $C^{10}H^8O = C^{10}H^7(OH)$ . *Reactions of  $\alpha$ -Naphthols with Polybasic acids, their Anhydrides and Chlorides* (J. Grabowski. *Deut. Chem. Ges. Ber.* iv. 661, 725; vi. 1065).— $\alpha$ -Naphthol, like other phenolic bodies, unites with many polybasic acids (or their anhydrides), with elimination of water, when the two bodies are heated together in presence of glycerin or sulphuric acid. The resulting compounds, which belong to the class of Baeyer's phenolic colouring matters, are not true ethers, but either compounds which retain the phenolic character of the naphthol, and dissolve in potash with a deep colour which disappears on reduction, or indifferent substances which may be regarded as the anhydrides of the former. The coloured compounds are designated, according to Baeyer's nomenclature, by names ending in *ein*, the reduced compounds by names ending in *in*.

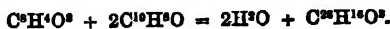
All these compounds are formed in such a manner that the OH-group of the acid unites with an atom of hydrogen from the naphthalene nucleus, forming water, which is eliminated, and the two residues unite together forming a ketonic compound. Thus carbonic acid forms with naphthol a compound having the formula,  $C^{10}H^{12}O^2$ :



*Phthalic acid* yields two compounds, viz.—



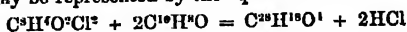
*Reaction with Phthalic Anhydride.*—When  $\alpha$ -naphthol is boiled with phthalic anhydride, the liquid acquires a dark green colour, and on exhausting the cooled mass with alcohol, there remains a white substance,  $C^{10}H^{10}O^3$ , which is the *anhydride* of naphthol-phthalcin (1):



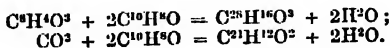
This compound separates from hot benzene in faintly yellowish crystals having a splendid vitreous lustre. It is insoluble in aqueous potash, and is converted by alcoholic potash into a green substance. Heated with sulphuric acid, it yields a red substance, which appears to have the composition  $C^{10}H^{10}O^4$ .

*With Phthalic Chloride.*—On heating a mixture of these two bodies on the water-bath, abundance of hydrogen chloride is evolved, and a green mass remains, partially soluble in cold dilute potash. The dissolved substance is purified by repeated fractional precipitation with hydrochloric acid and recrystallisation from benzene. The

small brown crystals so obtained dissolve in potash, with production of a fine blue colour; their composition, when dried at  $100^{\circ}$ – $110^{\circ}$ , is  $C^{22}H^{12}O^4 + \frac{1}{2}Aq$  (2). Leaving the half-molecule of water out of consideration, the formation of this body, called *phthalein- $\alpha$ -dinaphthol*, may be represented by the equation:

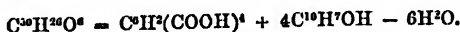


*With Oxalic Acid.*—On heating a mixture of oxalic acid, naphthol and sulphuric acid for two hours at  $100^{\circ}$ – $115^{\circ}$ , a dark mass is obtained only partially soluble in alkali; the portion insoluble is dissolved by hot benzene, and crystallises on cooling in colourless, warty groups. These are a mixture of various substances, but after oft-repeated recrystallisation they are converted into beautiful, colourless, glistening crystals of *carbonein- $\alpha$ -naphtholanhydride*,  $C^{21}H^{12}O^2$  (3). This body bears exactly the same relation to carbonic anhydride as the previously described phthalic compound does to phthalic anhydride:



The behaviour of the two substances is also identical (Grabowski, *loc. cit.*)

*With Pyromellitic Acid.*—The reaction between this acid and  $\alpha$ -naphthol is very complex, giving rise to a large number of compounds, the most important of which, from its analogy to the phthalic and carbonic acid compounds, is *pyromellitein-tetra- $\alpha$ -naphtholanhydride* (4):



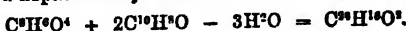
This compound is formed when one molecule of pyromellitic acid is heated with four molecules of  $\alpha$ -naphthol in an oil-bath to  $300^{\circ}$ . The product after being exhausted with boiling acetone and purified by fractional crystallisation from phenol, yields microscopic crystals, which have the composition  $C^{20}H^{20}O^6 \cdot C^8H^4OH$ , and lose their phenol when heated to  $260^{\circ}$ . From the mother-liquors the compounds are obtained, the first,  $2C^{20}H^{20}O^7 \cdot C^8H^4OH$ , in thin plates, the second in very slender needles; they lose their phenol when dried at  $260^{\circ}$ , and are reduced to  $\alpha$ - and  $\beta$ -*pyromellitein-tetra- $\alpha$ -naphtholhemianhydride*,  $C^{20}H^{20}O^7$ . In the acetone solution the compound  $\gamma$ -*pyromellitein-tetra- $\alpha$ -naphtholhemianhydride* is found. It melts at  $265^{\circ}$ , and when dried at  $150^{\circ}$  has the composition  $C^{20}H^{20}O^7$ . On heating one molecule of pyromellitic acid with three of  $\alpha$ -naphthol to  $250^{\circ}$  as long as water escapes, and removing the excess of naphthol by distillation in a current of aqueous vapour, a brownish-black mass is left. This, when purified by repeated solution in potash, precipitation by acid, and solution in ether, forms a brown powder, *tri- $\alpha$ -naphtholpyromelliteic acid* (6), which has the composition  $C^{16}H^{16}O^8$ , and is readily soluble in alcohol, ether, and acetone. It dissolves in alkalis with a deep green colour.

*Tri- $\alpha$ -naphtholhemianhydropyromelliteic acid*,  $C^{40}H^{22}O^7$  (7), is produced, together with the last-mentioned compound, when a mixture of one molecule of pyromellitic acid and three of  $\alpha$ -naphthol is heated to  $280^{\circ}$ – $300^{\circ}$ . It is a yellowish-brown powder, soluble with difficulty in cold alcohol or ether. It yields a fine blue solution with alkalis.

Pyromellitic anhydride and  $\alpha$ -naphthol fused together form a black resinous mass, which, when purified by solution in potash and fractional precipitation, yields *di- $\alpha$ -naphtholpyromelliteic acid* (8),  $C^{30}H^{18}O^8$ .

The formation of these several compounds is represented by the following equations:—

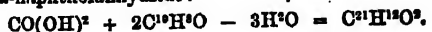
(1). Phthalein-di- $\alpha$ -naphtholanhydride:



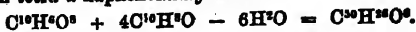
(2). Phthalein-di- $\alpha$ -naphthol:



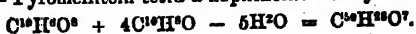
(3). Carbonein- $\alpha$ -naphtholanhydride:



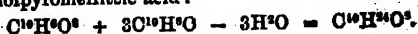
(4). Pyromellitein-tetra- $\alpha$ -naphtholanhydride:



(5).  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Pyromellitein-tetra- $\alpha$ -naphtholhemianhydride:



(6). Tri- $\alpha$ -naphtholpyromelliteic acid:

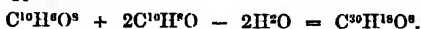




- (7). Tri-
- $\alpha$
- naphtholhemianhydridepyromellitic acid:



- (8). Di-
- $\alpha$
- naphtholpyromellitic acid:

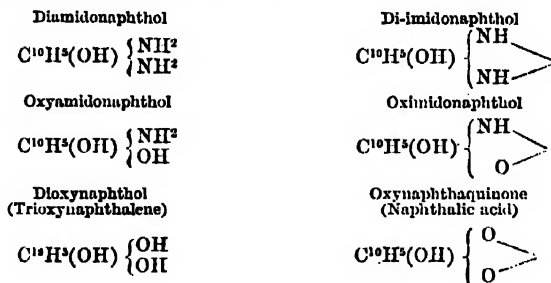


**Dinitronaphthols.** *Dinitro- $\alpha$ -naphthol*,  $C^{10}H^7(NO^2)^2OH$ , is formed by treating Dusart's nitroxynaphtholic acid (iv. 117) with dilute nitric acid, whence it may be inferred that Dusart's compound, to which he assigned the formula  $C^{10}H^7N^2O^4$ , is really mononitro- $\alpha$ -naphthol,  $C^{10}H^7NO^3 = C^{10}H^6(NO^2)OH$ . The latter melts at  $151^\circ$ – $152^\circ$ , not at  $100^\circ$ , as stated by Dusart (Darmstädter u. Nathan, *Deut. Chem. Ges. Ber.* 943).

*Dinitro- $\beta$ -naphthol*.—A solution of  $\beta$ -naphthol in a large quantity of alcohol is heated with dilute nitric acid, and the product, separated by water after the greater part of the alcohol has been removed by distillation, is purified by solution in dilute sodium carbonate, separation by hydrochloric acid, solution in alcohol, boiling with animal charcoal, reprecipitation by water, and finally by repeated crystallisation from chloroform.

*Dinitro- $\beta$ -naphthol*,  $C^{10}H^7(NO^2)^2OH$ , thus produced, crystallises in highly lustrous light yellow needles, which appear under the microscope as truncated prisms, and melt with brown coloration at  $195^\circ$ . It is very sparingly soluble in water, more soluble in alcohol, very soluble in ether and in chloroform. These solutions, as well as the salts, dye deep yellow. The ammonium salt crystallises in shining red needles, which decompose partially in contact with the air. The silver salt is a scarlet flocculent precipitate; the barium salt forms yellow needles which turn red at  $100^\circ$ . All these salts are very slightly soluble in water (Wallach u. Wichelhaus, *ibid.* 846).

**Amido- and Imido-naphthols.** These compounds, which were first obtained from dinitronaphthol by Martius u. Griess (1st *Suppl.* 857), have been further studied, together with some of their derivatives, by Græbe u. Ludwig (*Ann. Ch. Pharm.* cliv. 803), who infer from their results that these bodies have a quinonic constitution as indicated by the following formulæ:—



1. *Diamidonaphthol*,  $C^{10}H^{12}N^2O$ .—The free base has not been prepared. The *stannochloride*,  $C^{10}H^{12}N^2O \cdot 2HCl \cdot SnCl^2 + 2H^2O$ , is obtained by heating 1 part of dinitronaphthol with 2 parts of tin and 7.5 parts of hydrochloric acid, and crystallises from its aqueous solution by spontaneous evaporation in large monoclinic prisms. Another *stannochloride*, having the formula  $2(C^{10}H^{12}N^2O \cdot 2HCl) \cdot SnCl^2 + 4H^2O$ , is converted into the former by heating with stannous chloride. The *sulphate*,  $C^{10}H^{12}N^2O \cdot H^2SO^4 + H^2O$ , is formed when the solution of the base in hydrochloric acid is mixed with sulphuric acid. It dissolves easily in alcohol and in hot water, less easily in cold water. By the action of the air or of ferric chloride it becomes deep red, from formation of di-imidonaphthol.

2. *Di-imidonaphthol*,  $C^{10}H^{12}N^2O$ .—This base is best prepared by precipitating the solution of its hydrochloride with ammonia. It forms small needles, insoluble in cold water, easily soluble in alcohol. Heated with alcohol or water it gives off ammonia, and is converted into oximidonaphthol; reducing agents reconvert it into diamidonaphthol. It unites with acids, and is converted, by boiling with alkalis or by heating to  $120^\circ$  with dilute hydrochloric or sulphuric acid, into oxynaphthaquinone. The *hydrochloride*,  $C^{10}H^{12}N^2O$ , is prepared from the stannochloride of diamidonaphthol by precipitating the tin with zinc, adding ferric chloride, washing the hydrochloride of di-imidonaphthol thereby precipitated with dilute hydrochloric acid, and recrystallising it from water.

This salt is nearly insoluble in strong hydrochloric acid, but dissolves easily in

water and in alcohol, and separates from the aqueous solution by spontaneous evaporation in monoclinic prisms, which are dark red by transmitted light, and exhibit a green metallic lustre by reflected light. The *platinochloride* has the composition  $2(C^{10}H^7N^2O.HCl).PtCl^4$ . The *sulphate*,  $C^{10}H^7N^2O.SO^2H^2$ , forms red prisms having a metallic lustre.

3. *Oximidonaphthol*,  $C^{10}H^7NO^2$ , is obtained by boiling a hydrochloric solution of di-imidonaphthol, made alkaline with ammonia, as long as ammonia resulting from the decomposition of the di-imidonaphthol continues to escape. It forms yellowish-red needles quite insoluble in ether, nearly insoluble in cold water, slightly soluble in hot water, easily in alcohol. By boiling hydrochloric acid, boiling alkalis, or strong sulphuric acid, it is converted into naphthalic acid (oxynaphthaquinone); by reducing agents into oxyamidonaphthol.

4. *Oxamidonaphthol*.—The *hydrochloride*,  $C^{10}H^7NO^2.HCl$ , is formed by treating oximidonaphthol with tin and hydrochloric acid, and crystallises from the stanniferous solution in well-defined, very soluble tables; the solution alters quickly in contact with the air.

5. *Oxynaphthaquinone* or *Naphthalic acid*,  $C^{10}H^6O^4$ , is formed by heating di-imidonaphthol hydrochloride to  $120^\circ$ , with dilute hydrochloric or sulphuric acid (see NAPHTHAQUINONE, p. 836).

6. *Dioxynaphthol* or *Trioxynaphthalene*,  $C^{10}H^6O^2$ , is formed by reducing oxynaphthaquinone with tin and hydrochloric acid, and may be extracted from the liquid by ether after separation of the tin. It crystallises in yellow needles, is extremely oxidable, reduces silver and mercury salts, and alkaline cupric solution.

**Dinaphthols**,  $C^{20}H^{14}O^2 = (C^{10}H^7)^2O^2$  (Dianin, *Deut. Chem. Ges. Ber.* vi. 1252; vii. 125, 487). These compounds are produced by the action of ferric chloride on the aqueous solution of  $\alpha$ - or  $\beta$ -naphthol, ferrous chloride being formed at the same time, the solution assuming a rose-colour, and the dinaphthol separating in the solid state—



$\alpha$ -*Dinaphthol* forms small silvery rhombic plates melting at  $300^\circ$ . It strikes a red colour with ferric chloride and forms a violet precipitate with nitric acid. Treated with *benzoyl chloride* it yields dibenzoyl-dinaphthol,  $C^{20}H^{12}(C^7H^5O)^2O^2$ , which is insoluble in water and in alcohol, dissolves with difficulty in benzene, and crystallises out in warty masses made up of small rhombs. An alcoholic solution of caustic soda decomposes it completely into benzoic acid and  $\alpha$ -dinaphthol.

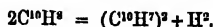
$\beta$ -*Dinaphthol* crystallises from alcohol in broad four-sided, pointed prisms, melting at  $218^\circ$ . It gives with ferric chloride a greenish colour, which on heating becomes red and brown; nitric acid colours it dark-green. On passing its vapour, mixed with air, through hot tubes, a yellow body, probably a naphthaquinone, is formed. With *benzoyl chloride* it forms the two compounds,  $C^{20}H^{12}(C^7H^5O)O^2$  and  $C^{20}H^{12}(C^7H^5O)^2O^2$ , the first crystallising in rhombic laminæ melting at  $204^\circ$ , the second in four-sided prisms which melt at  $180^\circ$ . Both are resolved by alcoholic potash into benzoic acid and  $\beta$ -dinaphthol. The formation of these two benzoic derivatives shows that the  $\beta$  compound from which they are derived, and therefore also the corresponding  $\alpha$  compound, is really a dinaphthol,  $C^{20}H^{14}O^2$ .

The two dinaphthols are insoluble in water, sparingly soluble in benzene and chloroform, freely in alcohol and ether. They also dissolve in alkalis, forming unstable salts. They are not changed by the action of tin and hydrochloric acid, but are converted into the mononaphthols when distilled.

**NAPHTHOPHTHALIC ACID**,  $C^{12}H^8O^4 = C^{10}H^7(CO^2H)^2$ . *Naphthalene dicarboxylic acid*.—This acid, which Darmstädter & Wichelhaus obtained by boiling dicyanonaphthalene with potash (1st Suppl. 852), is likewise produced by boiling acenaphthene with chromic acid mixture. It sublimes in broad, serrated plates, melting at  $286^\circ$ , and is precipitated by acids from its alkaline solution in slender needles, melting at the same temperature. Its *potassium salt*,  $C^{12}H^7K^2O^4 + 2H^2O$ , is precipitated by alcohol in small pearly plates. The *barium salt*,  $C^{12}H^6Ba^2O^4 + H^2O (2H^2O)$ , according to D. and W., is a precipitate consisting of small compact shining plates. The acid, heated to  $140^\circ$ – $150^\circ$ , is converted without melting into the anhydride,  $C^{12}H^6O^3$ . The calcium salt distilled with slaked lime yields naphthalene (Behr & van Dorp, *Deut. Chem. Ges. Ber.* vi. 80).

**NAPHTHYL**,  $C^{10}H^7 = C^{10}H^7.C^0H^1$ . Of this radicle in the free state two modifications are known, distinguished as *dinaphthyl* and *isodinaphthyl*. The former, discovered by F. Lossen, is produced by oxidising naphthalene with a mixture of manganese dioxide and dilute sulphuric acid (1st Suppl. 856). The latter, discovered

by Watson Smith (*Chem. Soc. J.* [2], ix, 1184), is obtained, together with hydrogen, by passing the vapour of naphthalene through an iron tube heated to bright redness:



The naphthalene collected in the receiver has a dark-brown colour, and, when re-distilled, from a retort, always leaves a minute quantity of liquid boiling at a temperature above  $360^{\circ}$ ; and by repeating the distillation a certain number of times, a quantity of this substance—which consists of impure isodinaphthyl—may be obtained sufficient for further treatment. It is purified by first distilling off the small quantity of naphthalene which it contains, and then distilling over the body itself, the temperature rapidly rising from  $220^{\circ}$ , below which the naphthalene comes over, to above  $360^{\circ}$ . A minute quantity of pitch is left in the retort. The solid, hard, yellowish substance is now crushed in a mortar with shale-spirit, and made into a thin homogeneous paste, then washed repeatedly on a filter with the spirit, drained, pressed in blotting-paper, and dried at a temperature fully sufficient to volatilise the spirit. By this washing it is freed from a small quantity of a resinous body, and from a lemon yellow substance. These wash-liquors all exhibit blue fluorescence. The dried substance is finally sublimed at as low a temperature as possible, and is then obtained as a faintly yellowish-white inodorous powder. This sublimate, by very careful and slow sublimation, may also be obtained in small, delicate plates. When possessing the faintest yellow tint, it imparts a beautiful and delicate-blue fluorescence to any liquid in which it is dissolved. When a very high temperature has been applied (a white heat), the substance obtained is always more largely contaminated with the resinous and lemon-yellow bodies, and on careful sublimation the first portions subliming are almost colourless, but the further the sublimation is carried on, the deeper is the yellow tint of the product. A small quantity of the latter portions of a sublimation-product of a sulphur-yellow colour, when warmed with concentrated sulphuric acid, yield a very fine purple solution, passing on further heating into an indigo and then to a dull green tint. This reaction is mentioned by Liebermann as characteristic of *chrysene*; probably, therefore, this yellow substance contains chrysono.

With a quantity of the pure re-sublimed substance the following results were obtained:—

No red or brown compound is formed with a benzol-solution of picric acid. The more thoroughly the substance is purified, the less is the fluorescence imparted to solvents.

Isodinaphthyl sublimes at a temperature considerably below its boiling point. Treated with two parts of potassium dichromate and sulphuric acid, it is oxidised at once with extreme energy. From the oxidation-product obtained, no colour, nor any substance bearing any resemblance to alizarin, could be obtained.

Sulphuric acid does not act on isodinaphthyl in the cold, but dissolves it when heated, forming, if the isodinaphthyl be quite pure, a very faint purplish-tinted solution; if, however, it contains a trace of the yellow body before mentioned, a violet or purple solution is formed, becoming green and then reddish-brown on further heating. The product is a sulpho-acid which forms a soluble barium salt. The sodium salt formed from it by double decomposition is very soluble in water, yielding a fluorescent solution.

Hot nitric acid oxidises isodinaphthyl with liberation of nitrous fumes, and forming in the hot liquid heavy oily drops; these on further heating dissolve in the acid, and a clear solution is obtained. On pouring this liquid into water, the nitro-compound is precipitated abundantly in a light yellow floccular form. Chlorine has no action upon it, when passed over it in a glass tube, and even on warming. When it is treated with bromine in the cold, a brominated compound is formed with very energetic action.

Chlorine passed over isodinaphthyl contained in a glass tube does not act upon it, even on application of heat; but when dry chlorine is passed through a solution of the substance in carbon sulphide, it is absorbed, with evolution of hydrochloric acid, and if, when the absorption is complete, the liquid be agitated with caustic soda solution, a gummy liquid is obtained which solidifies to a resinous mass soluble in ether and alcohol, and is precipitated from its alcoholic solution by water. The white precipitate washed and dried at  $100^{\circ}$  has the composition of tetrachlorisodinaphthyl,  $C_{20}H_4Cl_4$ .

Bromine acts violently on isodinaphthyl, with evolution of hydrobromic acid; and the product dissolved in carbon sulphide and purified as above exhibits the composition of heptabromisodinaphthyl,  $C^{10}H^7Br^7$  (Watson Smith & Poynting, *Chem. Soc. J.* [2], xii, 855).

The chief differences between dinaphthyl and isodinaphthyl are exhibited in the following table.

*Comparative behaviour of Dinaphthyl and Isodinaphthyl with Solvents, &c.*

Solvents	Loosen's Dinaphthyl	Isodinaphthyl	
	Solubility, Crystalline form, &c.	Solubility	Crystalline form, &c.
Proof spirit	—	Scarcely at all soluble, even on boiling with excess	On cooling, a few plates separate out
Ether	More soluble than in alcohol	Very slightly; less than in alcohol	In plates
Absolute alcohol	Less soluble than in ether; separates in moss-like clusters	Slightly in the cold; soluble on boiling	Beautiful rhomboïdal plates, which, on drying, overlap, and present a beautiful silky appearance. They have a very faint delicate greenish colour
Methylated spirit	—	Rather more soluble	Rhomboidal plates
Wood spirit	From ether-alcohol mixture; crystallises in octahedrons	—	
Light petroleum spirit, sp. gr. = 710	—	Still more soluble than in the above	Rhomboidal plates
Light shale spirit, sp. gr. = 737	—	Rather more soluble than in petroleum spirit	
Carbon tetrachloride	—	Not quite so soluble as in benzene	Fine large fluorescent plates having when dry a silky laminated appearance
Benzol	About the same as in alcohol	Sparsely in the cold, freely in the hot fluid	
Carbon disulphide	Easily soluble	Easily soluble, even in the cold	In plates
Oil of turpentine	—	Very easily soluble	Delicate white lance-shaped crystals
Chlorine	Forms $C^{20}H^{10}Cl^4$	Forms $C^{20}H^{10}Cl^4$	
Bromine	" $C^{20}H^{10}Br^2$ and $C^{20}H^{10}Br^4$	" $C^{20}H^{10}Br^2$	
Melting point	154°	204°	
Boiling point	above 360°	above 360°	

**NAPHTHYL ALCOHOLS.** See NAPHTHOLS (p. 830).

**NAPHTHYL CYANATE**,  $CONC^{10}H^7$ , formerly obtained in small quantity by heating dinaphthylcarbamide with phosphoric anhydride (iv. 19), is more easily produced by similar treatment of naphthyl-urethane,  $CO \{NH(C^{10}H^7)\}$ . It is a colourless liquid, having a faint odour and boiling at 280°–270°. It reacts energetically with water, alcohols, and amines, and solidifies instantly with triethylphosphine (Hofmann, *Proc. Roy. Soc.* xix. 108).

**NAPHTHYL SULPHIDES** (H. E. Armstrong, *Deut. Chem. Ges. Ber.* vii. 407):  $\alpha$ -naphthyl sulphide,  $(C^{10}H^7)^2S$ , is obtained on distilling a dry mixture of potassium sulphocyanate and  $\alpha$ -naphthalene-sulphonate. It crystallises in long white needles, difficultly soluble in alcohol, but very soluble in carbon sulphide and glacial acetic acid. It melts at about 100°. The corresponding  $\beta$ -naphthyl sulphide appears to be formed when  $\beta$ -naphthalene is distilled with potassium sulphocyanate. It has a higher melting point and is less soluble than  $\alpha$ -naphthyl sulphide.

**NAPHTHYLACETAMIDE** or **ACETONAPHTHYLAMINE**,  $C^{10}H^7NH(C^2H^3O)$  (Rother, *Deut. Chem. Ges. Ber.* iv. 850; Tommasi, *Compt. rend.* lxxvi. 1287). This compound is produced by treating naphthylamine with acetyl chloride, acetic anhydride, or glacial acetic acid, most conveniently with the last (Tommasi); by heating naphthylamine with glacial acetic acid for several days (Rother). It crystallises in white silky needles melting at  $152^\circ$  and subliming at  $160^\circ$  (Tommasi); melts at  $150^\circ$  (Rother). It is only slightly soluble in boiling water, but dissolves easily in alcohol and in dilute acids (Tommasi).

**Naphthylchloracetamide**,  $C^{10}H^7NH(C^2H^2ClO)$ , prepared by the action of chloroacetyl chloride on naphthylamine, crystallises in colourless silky needles melting at  $121^\circ$ , soluble in alcohol and in acetic acid (Tommasi).

**Bromonaphthylacetamide**,  $C^{10}H^6BrNH(C^2H^3O)$ , formed by passing bromine through naphthylacetamide suspended in carbon sulphide, is a heavy amorphous substance melting at  $94^\circ$ . By boiling with strong potash-ley it is converted into monobromonaphthylamine,  $C^{10}H^6BrNH_2$ ; and on converting the latter into the corresponding diazo-compound, and heating this diazo-compound with alcohol, a monobromonaphthalene is obtained which, from its boiling-point ( $277^\circ$ ), melting point, and the crystalline forms of its derivatives, appears to be identical with the bromonaphthalene obtained by the direct action of bromine upon naphthalene (Rother).

**Dinitronaphthylacetamide**,  $C^{10}H^6(NO_2)_2NH(C^2H^3O)$ , is precipitated as a yellow mass from a solution of naphthylacetamide in cold fuming nitric acid (Rother).

**NAPHTHYLAMINE**,  $C^{10}H^7N = C^{10}H^7NH_2$ . For the preparation of this base from nitronaphthane, Ballö (*Deut. Chem. Ges. Ber.* iii. 288, 673) recommends Réchamy's method of reduction with iron and acetic acid at a moderate heat, with this difference, however, that the product, after reduction, is to be supersaturated with soda-ley and distilled with steam, with the aid of good condensation.

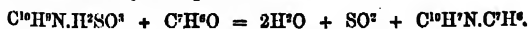
For Böttger's mode of preparation with zinc and hydrochloric acid, see 1st Suppl. 861.

Naphthylamine, heated to boiling with dry ethyl oxalate, yields ethyl naphthyl-oxamate; but when heated to  $90^\circ$  with the same ether in presence of alcohol, it is converted into naphthylammonium naphthylloxamate. See NAPHTHYLOXAMIC ACID (p. 848).

**Naphthylamine Bisulphite**,  $C^{10}H^7N.H^2SO_3$ , is prepared by passing a stream of sulphur dioxide into water containing naphthylamine in suspension, assisting the action by a gentle heat and frequent agitation. The base then slowly dissolves, and the solution, on cooling, leaves the bisulphite in white rosettes having a nacreous lustre. This salt does not become coloured on exposure to light so readily as other salts of naphthylamine; neither does it decompose if kept in the solution saturated with sulphurous acid, but if taken out and quickly dried, it gives up its sulphurous acid and leaves pure naphthylamine. This decomposition may perhaps afford an easy method of obtaining the base pure and white.

Naphthylamine bisulphite unites with aldehydes, forming compounds analogous to those of the aldehydes with the bisulphites of aniline, phenylamine, &c. (1st Suppl. 79, 920).

**Benzoyl-bisulphite of Naphthylamine**,  $C^{10}H^7N.H^2SO_3.C^7H^5O$ , is formed on pouring benzoic aldehyde into a hot aqueous solution of naphthylamine bisulphite, and separates, on cooling, in ramified groups of small crystals which, if dried and placed in a well-closed vessel, may be kept for a long time without sensible alteration. It dissolves in alcohol, but not in ether or in water. This compound, when gently heated, gives off the whole of its sulphurous acid, leaving a resinous, very fusible compound, very soluble in ether, moderately soluble in absolute alcohol, insoluble in water. The ethereal solution, mixed with alcohol of ordinary strength, deposits the compound as a whitish-yellow crystalline powder having the composition  $C^{10}H^7N.C^7H^5$ . Its formation may be represented by the equation:

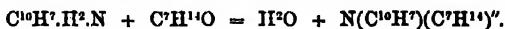


It does not unite with acids or with platinum chloride.

Naphthylamine bisulphite unites also with *cumic*, *cinnamic*, *salicylic*, and *anisic aldehydes*, forming crystalline compounds analogous to the benzoic compound above described.

With the aldehydes of the fatty series, on the contrary, similar compounds are not obtained. *Acetic aldehyde* acts very strongly on naphthylamine bisulphite, producing resin of aldehyde. *Butyric*, *valeric*, and *amanthyl* aldehydes form resinous garnet-red compounds, liquid at first, but afterwards solidifying to very friable crystalline masses, very soluble in ether and absolute alcohol.

The cenanthylic compound thus obtained gave by analysis 82.79 and 83.2 p.c. carbon, 9.1 and 9.8 hydrogen, agreeing approximately with the formula  $C^{10}H^{12}N$ , or  $N\{(C^1H^1)^7\}$ , which requires 85.37 C. and 8.79 N. It appeared to be contaminated with a small quantity of a sulphuretted compound. The same compound is formed with separation of water, when a solution of naphthylamine in anhydrous ether is mixed with cenanthol:



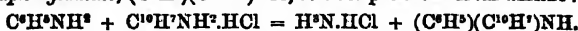
It does not possess basic properties.

Acetone does not act on naphthylamine bisulphite (G. Papasogli, *Gazzetta chimica italiana*, iii. 394).

*Substitution-derivatives of Naphthylamine.*

Girard a. Vogt (*Bull. Soc. Chim.* [2], xviii. 67) have obtained several secondary monamines containing naphthyl by heating a primary monamine with hydrochloride of naphthylamine to  $280^{\circ}$ – $300^{\circ}$  in a closed vessel for 30 hours.

Phenyl-naphthylamine,  $(C^6H^5)(C^{10}H^7)NH$ , is thus produced from aniline:—



From the products of the reaction, the phenyl-naphthylamine is isolated by treatment with water, which leaves the base as an oily liquid which soon solidifies; by washing, pressure between bibulous paper, and crystallisation from alcohol, it is obtained in small crystals fusible at  $60^{\circ}$ , and soluble in alcohol, benzene, and ether, its solutions exhibiting dichroism; it distils unchanged at about  $315^{\circ}$  under 528 mm. pressure.

Its hydrochloride is obtained in small crystals by passing hydrochloric acid gas into a solution of the base in benzene; by ebullition of the benzene liquid it is mostly decomposed; alcohol also partly decomposes it, whilst water resolves it wholly into hydrogen chloride and the free base.

Cresyl-naphthylamine,  $(C^6H^7)(C^{10}H^7)NH$ , is similarly obtained by the action of toluidine on naphthylamine hydrochloride at  $280^{\circ}$  for 36 hours; it melts at  $79^{\circ}$  and distils at  $290^{\circ}$  under 528 mm. pressure, and at  $236^{\circ}$  under 15 mm. pressure. Its hydrochloride is obtained by the same means as those used for phenyl-naphthylamine, and is also decomposed by water.

A base isomeric with cresyl-naphthylamine is formed by treating naphthylamine with benzyl chloride in presence of a small quantity of zinc-dust. It has a deep brown colour, and is uncrystallisable, but may be obtained in scales like those of potassium ferriate tartrate. With fuming nitric acid it forms a yellow nitro-derivative (Froté a. Tommasi, *Compt. rend.* lxxvii. 57).

Xylynaphthylamine,  $\left. \begin{smallmatrix} C^8H^7 \\ H \end{smallmatrix} \right\} N$ , has not been obtained solid, but in the form of a viscous liquid, rapidly becoming brown, and boiling at  $243^{\circ}$ – $245^{\circ}$  (15 mm. bar.) It is no doubt a mixture of isomeric bodies, arising from the isomeric xylenes contained in the hydrocarbon boiling at  $130^{\circ}$ .

Dinaphthylamine,  $\left. \begin{smallmatrix} C^{10}H^7 \\ C^{10}H^7 \\ H \end{smallmatrix} \right\} N$ , prepared by heating naphthylamine hydrochloride with naphthylamine, forms crystals, apparently quadratic, with truncated edges. It melts at  $113^{\circ}$ , and boils at about  $310^{\circ}$ – $315^{\circ}$  (15 mm. bar.)

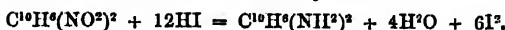
**NAPHTHYLAMINE VIOLET.** A. Kielmayer (*Dingl. polyt. J.* cxvii. 67) prepares this colouring matter for calico-printing by boiling together 456 grams of starch, 1.1 litre of water, and 118 grams of dry naphthylamine dissolved in 1.5 litre of water and 70 grams of hydrochloric acid of sp. gr. 1.12, and adding to the liquid, after cooling, 13.5 grams of potassium chlorate dissolved in 0.3 litre of water. The printed goods are hung for three days in the oxidising room, then drawn through a soda-bath, and finally through a soap-bath, whereby their grey colour is developed into the pure violet shade; this, however, is much influenced by the temperature of the oxidation-room, and of the dry rollers, &c. Naphthylamine violet does not appear to be the final product of a chemical process, like aniline-black, but merely a transition-stage.

According to A. Scheurer (*ibid.* cxvii. 443), the dirty-gray violet with which the fabrics issue from the oxidising-room is changed by alkalis into a purer violet, partially decolorised by tin-salt, and turned gray by a boiling solution of tin-salt, and by sulphurous acid. Dilute acetic acid does not affect the colour; potassium chromate and solution of chloride of lime turn it brown. The oxidation goes on most regularly when the oxidising-chamber is kept cold and contains vapours of acetic acid. Scheurer

likewise regards the violet as only an intermediate stage of the oxidation, and attributes the beneficial action of the acetic acid to retardation of the oxidation which it effects.

Blumer-Zweifel (*ibid.* cxcvi. 66) produces naphthylamine violet directly on the fibre, by printing linen or cotton stuffs with a solution containing, in a litre of suitable thickening material, 30 grams of naphthylamine hydrochloride and 15 grams of cupric chloride solution of 15 B. For dyeing, the thickening material is omitted, and the quantity of cupric chloride reduced by a fourth. If only 15 grams of naphthylamine salt are used in the mixture, light shades are produced; 45 grams, on the other hand, produce dark shades. The printed or dyed stuffs are left for two or three days in the oxidising-chamber at a temperature of 25 C., and the colours are fixed by washing with soap-water. Alkaline baths render the colour reddish; acid baths make it bluish.

**NAPHTHYLENE-DIAMINES**,  $C^{10}H^8N^2 = C^{10}H^8(NH^2)^2$  (A. de Aguiar, *Dent. Chem. Ges. Ber.* iii. 27). These bases,  $\alpha$  and  $\beta$ , are formed by the action of phosphorus iodide on the corresponding dinitronaphthalenes. The dinitronaphthalene must be pulverised, and only a small quantity of water added; the reaction then goes on quickly, and the resulting naphthylene-diamine, which is almost insoluble in the acid liquid, is precipitated in the form of small crystals:



The di-hydriodide of  $\beta$ -naphthylene-diamine,  $C^{10}H^8(NH^2)^2 \cdot 2HI$ , is not a very stable compound. When gently heated it gives off hydriodic acid, and is converted into the mono-hydriodide. According to Costa, it crystallises in the rhombic system, exhibiting the combination  $OP \cdot \infty Pn \cdot \infty P \cdot \infty P \infty$ . The crystals are small prisms with rectangular base, the longer sides of which are slightly truncated; they are transparent with a faint fatty lustre and white colour inclining to straw-yellow; cleavable parallel to the faces of a rhombic prism. When well-defined and neutral they dissolve readily in water, but the solution turns red when heated and decomposes after a while. Free hydriodic acid diminishes the solubility, but increases the stability of the compound. The salt dissolves freely in alcohol, and may be obtained, by evaporation of the aqueous or alcoholic solution, in finely-developed but somewhat coloured crystals. When dry it changes colour by keeping, or under the influence of light, to yellow and red, and finally to black, but may for the most part be regenerated by treatment with hydriodic acid. The dry salt is decomposed by heat, giving off iodine and hydrogen iodide, while a sublimate and a brown oil distil over, and a carbonaceous residue is left behind. It reduces silver and platinum salts. Alkalis form with it a whitish precipitate which becomes coloured in contact with the air and melts to globules when heated. Oxalic acid produces no reaction in cold dilute solutions, but on evaporating to a certain degree of condensation, a red precipitate is obtained which becomes fiery-red on exposure to the air (this reaction is characteristic of the  $\beta$  base). *Sulphate of  $\beta$ -naphthylene-diamine* separates, when a strong solution of the preceding salt is mixed with sulphuric acid, in small white crystals, which may be purified by washing with dilute sulphuric acid, then with alcohol and ether. The salt is soluble in water, and is precipitated from its solution by the fixed alkalis, the precipitate redissolving in ammonia. It is precipitated without alteration by strong nitric, hydrochloric, and sulphuric acid. Fuming nitric acid blackens the liquid and forms a black precipitate. Potassium hypochlorite forms a blue precipitate turning red in contact with the air. Potassium nitrite forms immediately a cinnabar-coloured precipitate insoluble in hot water, soluble with yellow-red colour in alcohol or ether. The *hydrochloride of  $\beta$ -naphthylene-diamine*,  $C^{10}H^8(NH^2)^2 \cdot 2HCl$ , may be prepared by decomposing the sulphate with barium chloride, or better by precipitating the hydriodide with fuming hydrochloric acid, and purified by crystallisation, or by washing with dilute hydrochloric acid, and drying on a porous tile. It is more stable than the hydriodide; when heated in the dry state, it gives off hydrogen chloride, and yields a sublimate, with a residue of difficultly combustible charcoal. In other respects it resembles the preceding salts, excepting that potassium hypochlorite immediately produces with it a black precipitate, and slight reddening of the liquid, whereas with the sulphate this reaction takes place only after acidulation with hydrochloric acid.

*$\alpha$ -Naphthylene-diamine hydriodide* is prepared like the  $\beta$ -salt, but crystallises better from water than from alcohol. In most of its properties it closely resembles the  $\beta$ -salt. According to Costa the crystals are monoclinic, having the angle of the inclined axes equal to  $80^\circ$ , and exhibiting the combination  $OP \cdot \infty P \cdot \infty P \infty \cdot (\infty P \infty)$ . The crystals form small thin tables, appearing under the microscope as oblique prisms with rhombic or rhomboidal base, the plane angles of which differ but little from  $90^\circ$ . They are semi-transparent and brittle. The *sulphate*, prepared like the  $\beta$ -salt, crystallises in thin white needles. In its aqueous solution potassium hypochlorite produces

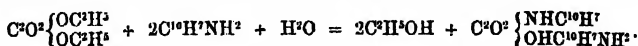
# 848 NAPHTHYLOXAMIC ACID—NAPHTHYL-URETHANE.

a fine violet coloration, changed to red by excess of the reagent, while red flocks are deposited. On addition of hydrochloric acid the liquid resumes its former colour; the precipitate which is then formed becomes darker on exposure to the air. Fuming nitric acid produces a red colour; potassium nitrite produces the same effect in dilute solutions, but in concentrated solutions still containing crystals it produces a violet colour and a violet precipitate which becomes darker on exposure to the air. The hydrochloride of  $\alpha$ -naphthyleno-diamine crystallises in prisms and exhibits the same reactions as the sulphate, excepting that it gives an immediate violet precipitate with potassium hypochlorite and likewise with chlorine-water.

**NAPHTHYLOXAMIC ACID**,  $C^{10}O^2 \begin{Bmatrix} NHC^{10}H^7 \\ OH \end{Bmatrix}$  (Ballò, *Deut. Chem. Ges.*

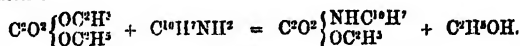
*Ber.* vi. 247). Ethers of this acid are produced by the action of ethyl oxalate on naphthylamine, the action being different according as it takes place between the dry substances or in presence of alcohol.

When 1 mol. of ethyl oxalate is heated to  $90^\circ$  with 1 mol. (or better with 2 mol.) of naphthylamine and a little 90 p.c. alcohol in a sealed tube for two or three hours, the product is naphthylammonium naphthylloxamate, formed according to the equation:



Naphthylammonium naphthylloxamate crystallises from alcohol, and better from hot water, in dry, fine, white needles, which melt at  $154^\circ$ , undergoing rapid decomposition. It is soluble in chloroform, carbon sulphide, and ether. Warm dilute hydrochloric acid dissolves and decomposes it, setting free naphthylloxamic acid. The aqueous solution gives with calcium chloride a precipitate of calcium naphthylloxamate.

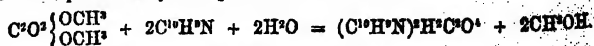
When, on the other hand, naphthylamine is heated to boiling for some time with excess of dry ethyl oxalate, and the product, after cooling, is exhausted with boiling alcohol, the solution thus formed deposits crystals of ethyl naphthylloxamate, whilst the undissolved residue consists of a white pulverulent substance nearly insoluble in ordinary solvents, melting at  $231^\circ$ , and subliming at a somewhat higher temperature in delicate, white, often iridescent, crystals. The reaction in this case is represented by the equation:



Ethyl naphthylloxamate crystallises from alcohol in needles. It melts at  $106^\circ$ . It appears to be insoluble in water, but dissolves easily in chloroform and carbon sulphide, sparingly in ether.

Free naphthylloxamic acid,  $C^{10}O^2 \begin{Bmatrix} NHC^{10}H^7 \\ OH \end{Bmatrix}$ , is obtained by dissolving the foregoing naphthylammonium salt in hot weak hydrochloric acid, from which solution it crystallises in tufts of fine white needles. It dissolves easily in alcohol, less freely in ether, and with difficulty in water. It melts at  $180^\circ$ , undergoing decomposition. Its salts decompose when heated, evolving vapours which smell strongly of naphthylamine, and leaving a residue of carbon. The potassium salt is obtained by dissolving the acid in hot solution of potassium hydrate, not too strong. It is deposited, on cooling, in beautiful anhydrous crystals. The barium salt, obtained by saponifying the ethyl-compound with baryta-water, is a white crystalline powder, insoluble in water. The calcium salt is obtained by adding calcium chloride to a solution of the naphthylammonium salt.

When alcoholic solutions of 1 mol. of methyl oxalate and 2 mol. of naphthylamine are mixed at ordinary temperatures, a mass of crystals is formed consisting, not of a derivative of oxamic acid, but of naphthylamine oxalate. The crystals when heated give off carbon oxide and dioxide, and naphthylamine, whilst Zinin's oxanaphthalide and formamide are produced. The reaction between methyl oxalate and naphthylamine is represented by the equation:



**NAPHTHYL-PHENYLAMINE.** See PHENYL-NAPHTHYLAMINE (p. 846).

**NAPHTHYL-PHENYL-GUANIDINE.** See GUANIDINE (p. 583).

**NAPHTHYL-PHENYL KETONE.** See PHENYL KETONES.

**NAPHTHYL-PURPURIC ACID.** See PURPURIC ACID.

**NAPHTHYL-URETHANE.** See CARBAMATES (p. 263).



**NARCEINE.** On the detection of this alkaloid in chemo-legal investigations, see F. Salomon (*Zeitschr. anal. Chem.* x. 454; *Chem. Soc. J.* [2], x. 331).

**NARCOTINE.** See OPIUM ALKALOIDS.

**NATALOIN.** The aloin of Natal aloes (p. 53).

**NEPHERITE.** Recent analyses of this mineral from various localities lead to the conclusion that all nephrites consist essentially of a calcium-magnesium silicate (granatitic or tremolite), the variations in the analytical results being due to the presence of small quantities of other minerals (Fellenberg, *Jahrbuch. f. Mineralogie*, 1871, 173; Konngott, *ibid.* 293; *Chem. Soc. J.* [2], ix. 324, 673).

**NICKEL.** *Atomic Weight.*—R. H. Leo (*Sill. Am. J.* [3], ii. 44) has determined the atomic weight of this metal by the analysis of its crystalline double cyanides with strychnine and brucine. These compounds, prepared in the same way as the corresponding cobalt salts (p. 362), have the formulae  $\text{Ni}^{2+}\text{C}_2\text{H}_2(\text{C}^{2-}\text{H}^{2-}\text{N}^{2-}\text{O}^{2-})\text{H}^{+} + 10\text{H}_2\text{O}$  and  $\text{Ni}^{2+}\text{C}_2\text{H}_2(\text{C}^{2-}\text{H}^{2-}\text{N}^{2-}\text{O}^{2-})\text{H}^{+} + 8\text{H}_2\text{O}$ . Six analyses of the brucine salt gave, for the atomic weight of nickel, numbers between 57.79 and 58.20; mean 57.98; and six analyses of the strychnine salt gave 57.72–58.21; mean 58.04. The mean of the whole is 58.01, or very nearly 58, which is considerably below the number determined by Russell (*1st Suppl.* 865), viz., 58.70.

*Occurrence.*—Nickel-linnæite, or Siegenite (iv. 44), containing 30 p.c. nickel, has been found in the mine of La Motte in Missouri, already known for its richness in copper, lead, and iron ores.

*Reaction of Nickel and its Oxides with the Oxides of Carbon.*—Nickel monoxide heated in carbon monoxide is reduced, with separation of carbon, to a compound whose proportion of oxygen agrees with the formula  $\text{Ni}^2\text{O}$ . In this respect nickel acts like iron (p. 259). Nickel sesquioxide is reduced to metallic nickel, with separation of a large quantity of carbon. Metallic nickel, heated in carbon monoxide, separates only a small quantity of carbon, and remains for the most part unaltered. Spongy metallic nickel, heated for 40 minutes to low redness in carbon dioxide, gave off 40 c.c. gas, 90 p.c. of which consisted of the monoxide. In the gases evolved by the decomposition of oxalic acid this kind of nickel remained unaltered (L. Bell, *Chem. News*, xliii. 258).

*Reaction with Ammonium Sulphide.*—Nickel immersed in yellow ammonium sulphide combines with the sulphur and colours the alkaline sulphide, eventually turning it deep black. Cobalt, on the other hand, is but very slightly acted on, even after several months' immersion (E. Priwoznik, *Ann. Ch. Pharm.* clxiv. 46).

*Fatination and Separation.*—On the estimation of nickel by electrolytic precipitation, see Merrick (*Chem. News*, xxiv. 100; *Chem. Soc. J.* [2], ix. 1091).

The several methods proposed for the separation of nickel from zinc have been examined by Klavo a. Deus (*Zeitschr. anal. Chem.* 1871, 190; *Chem. Soc. J.* [2], ix. 955). They give the preference to the method of Smith a. Brunner (*Dingl. pol. J.* cl. 369), which consists in passing sulphuretted hydrogen through a very dilute solution of the two metals in hydrochloric or nitric acid (1 gram of the oxides to at least 500 grains of liquid), nearly saturated with sodium carbonate; and when a large portion of the zinc is precipitated, adding a few drops of a very dilute solution of sodium acetate, which precipitates the whole of the zinc sulphide; filtering after 10–12 hours; and finally precipitating the nickel with potash after expelling the sulphuretted hydrogen. Klavo a. Deus observe that the saturation of the free acid in the solution of the two metals must be very carefully performed, so that only a trace of free acid may remain, as otherwise the precipitation of the zinc will not be complete; care must also be taken to add only a very small quantity of sodium acetate, as the least excess of this salt gives rise to precipitation of the nickel on subsequently passing sulphuretted hydrogen through the liquid.

On the distinction of nickel from manganese, zinc and cobalt by means of sodium sulphocyanate and potassium ferrocyanide, see COBALT, p. 362.

*Electrolytic Deposition of Nickel.*—To precipitate nickel in dense layers capable of receiving a good polish, Isaak Adams (*Compt. rend.* lxx. 123, 137) uses a bath containing only sulphate or chloride of nickel and ammonium, and free from every trace of fixed alkalis, as the presence of these latter gives rise to the formation of nickel peroxide. According to E. and Ch. Becquerel, on the other hand (*ibid.* 124, 137, 181), the formation of peroxide may be prevented by continual addition of ammonia, to neutralise the acid as fast as it is set free by deposition of the nickel, in which case the double sulphate of nickel and potassium will also give a dense metallic precipitate. E. Gaiffe, on the contrary (*ibid.* 181), defends Adams's view, observing that, to keep the bath in a proper degree of concentration by means of an anode of nickel, it is

2nd Sup.

necessary that only ammonium double salts be present. The use of metallic nickel as anode is also recommended by Jacobi (*ibid.* 1886) and Remington (*Dingl. polyt. J.* exev. 374).

The following method for the electrolytic deposition of nickel on wrought iron, cast iron, steel, copper, brass, zinc, and lead is given by F. Stolba (*Dingl. pol. J.* ccl. 145). A saturated solution of zinc chloride is mixed in any convenient vessel, best in a copper kettle, with about twice its volume of water; the solution is heated to boiling, and any turbidity that may arise is removed by addition of hydrochloric acid. The objects to be coated with nickel, after being carefully cleansed, are immersed in the zinc solution, and on adding to the boiling solution a little pulverised zinc, they become coated with a thin layer of zinc, to which the nickel adheres well. Nickel sulphate or potassium-nickel sulphate in the solid state or in solution is then added to the boiling liquid till it exhibits a green colour, a few cuttings of zinc are added, and the boiling is continued. If care be taken that the liquid remains clear, a closely adhering yellow deposit of nickel is obtained, shining or dull according as the metal surface on which it is deposited is polished or unpolished.

Cobalt may be precipitated upon metals in the same manner, but the deposit is not so beautiful as that of nickel, and is more easily attacked by the air.

An apparatus for coating the inside of metal tubes with nickel is described by Towle (*Engineering*, May 1871, p. 369).

**Alloys.** The following alloys of nickel have been analysed by A. Rüssler (*Chem. News*, xxi. 218).

	1	2	3	4	5	6
Copper . .	88.00	65.0	43.8	40.4	55.0	50.0
Nickel . .	8.75	16.8	15.6	31.6	20.0	25.0
Zinc . .	—	13.0	40.6	25.4	25.0	25.0
Iron . .	1.75	3.4	—	2.6	—	—

No. 1 is so-called *white copper*, which has been prepared in Suhl for about 100 years. No. 2 is an alloy from Paris distinguished by its capacity for polishing and gilding. Nos. 3 and 4 are Chinese *packfongs*. No. 5 is used for knife-handles, and 6 for forks. In many countries alloys containing nickel are used for small coins. Thus the Swiss pieces of 20, 10, and 5 centimes contain nickel and zinc in the proportion of 1 : 1.25, together with copper and silver. In the United States small coins are used containing 88 p.c. copper to 12 p.c. nickel.

Small crystals lining the cavities of a mass which had collected on the hearth of a nickel-smelting furnace, used for the roasting of magnetic pyrites containing 2 p.c. nickel and cobalt, were found by J. Wharton (*Sill. Am. J.* [2] xlix. 365) to have the composition A; the granular ground-mass had the composition B.

	Cu	Ni and Co	Fe	S
A.	1.85	25.22	64.10	8.00
B.	1.74	28.20	62.50	7.60

Some of the crystals were cubes, others were octohedrons grouped in spikes or dendrites.

**Oxides and Hydrates.** According to H. Teichmann (*Ann. Ch. Pharm.* clvi. 77) the nickel hydrate precipitated by caustic soda from the chloride or sulphate, obstinately retains small portions of acid; to obtain the hydrate quite pure it must be precipitated from the nitrate with caustic soda quite free from carbonate, and washed first with cold water till all alkaline reaction has disappeared, then with ammoniacal water, and finally with boiling water to remove any fixed alkali still adhering to it.

According to W. Wernicke (*Pogg. Ann.* cxli. 109) nickel peroxide precipitated by electrolysis from a neutral or alkaline solution, is a hydrate having the composition,  $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , and specific gravity = 2.744.

On the *Chromates of Nickel*, see CHROMIUM (p. 335).

**Sulphides** (K. Liebe, *Jahrbuch f. Mineralogie*, 1871, 840).—Two sulphides of nickel have lately been obtained from a mine in the Westerwald, viz. millerite, or capillary pyrites,  $\text{NiS}$  (iv. 42), and beyrichite, a mineral not previously known.

Beyrichite forms radiate groups of macle crystals, made up of prisms about 70 mm. long and 8 mm. thick, some of which have a helicoidal curvature. The prismatic groups have mostly a single end-face, inclined at  $81^\circ$  to the vertical axis. A second but somewhat rarely occurring end-face, forms with the first a dome-like combination, with an angle of  $144^\circ$  corresponding with the angle of the terminal edges of millerite. Cleavage moderately distinct, parallel to the first-mentioned end-face.

The mineral belongs to the family of the glances rather than to that of the pyrites. It is very tough, but moderately impressionable to the point of a knife. Hardness

about 3.2 to 3.3. Sp. gr. 4.7. Colour, red-grey, with faint metallic lustre, stronger on the cleavage-faces. When heated in a tube, it decrepitates, and at a dull red heat, gives off sulphur, without fusion, and is thereby converted into a pyrites, having a dark pinchbeck-brown tarnish on the surface, spess-yellow to brass-yellow internally, harder and more brittle than the original mineral. On charcoal, beyrichite melts easily and quietly, with evolution of sulphurous acid, to a strongly magnetic bead, having a brass-yellow colour internally. It gives the nickel reaction with borax and phosphorus salt, and dissolves easily in hydrochloric acid, especially on addition of nitric acid, forming an emerald-green solution. Pure specimens yield by analysis 42.86 p.c. sulphur, 2.70 iron, and 54.23 nickel. If the iron be supposed to replace an equivalent quantity of nickel, these numbers lead to the formula  $\text{Ni}^{25}\text{S}^7$  or  $3\text{NiS}.2\text{NiS}^2$  (calc. 43.21 S, and 56.79 Ni). The presence of the iron may, however, be due to the admixture of iron pyrites, and in that case the composition of beyrichite may be represented by the formula  $2\text{NiS}.2\text{NiS}^2$ .

The crystals of beyrichite are coated by millerite in extremely thin yellow laminae, or more rarely in dendritic or thin crystalline forms, often penetrating them in the direction of the cleavage-planes, in the form of sharply separated lamellae, sometimes to the complete displacement of the beyrichite. The millerite has a sp. gr. of 5.7 to 5.9, hardness between 3.6 and 3.8, and contains 35.27 p.c. S, 1.16 Fe, and 63.41 Ni.

Beyrichite, as appears from the facility with which it gives off sulphur when heated, is very easily converted into millerite, a circumstance which may perhaps account for the great variations in the statements respecting the specific gravity and other properties of the latter (i. 42). These diversities may be due either to the presence of beyrichite enclosed in the capillary pyrites, or to the different conditions under which the transformation of beyrichite into millerite takes place. Beyrichite is, in fact, converted into millerite by taking up nickel from the vein-water, and the more compact and less porous the structure of the beyrichite, the denser and heavier will be the millerite formed from it.

*Nickel-gyauite* or *Genthite*.—This mineral was originally found as a yellow-green incrustation on chromo-iron ore at Texas, Lancaster Co., Pennsylvania, and was examined by Genth (*Kenngott's Uebersicht*, 1852, 45), who found it to have a sp. gr. of 2.49, and to contain—

$\text{SiO}^2$	$\text{NiO}$	$\text{MgO}$	$\text{FeO}$	$\text{CaO}$	$\text{H}^2\text{O}$
35.36	30.64	14.60	0.24	0.26	19.09 = 100.19

agreeing approximately with the formula—



A different composition has been deduced by P. F. Dunnington (*Chem. News*, xxv. 290) from the analysis of a specimen from the neighbourhood of Webster (sp. gr. 2.48), which gave—

$\text{SiO}^2$	$\text{NiO}$	$\text{MgO}$	$\text{FeO}$	$\text{H}^2\text{O}$
49.89	22.35	16.60	0.06	12.36 = 101.26

numbers which are most nearly represented by the formula—



**NICOTINE**,  $\text{C}^4\text{H}^7\text{N}$ . *Occurrence in Tobacco*.—According to Vohl a. Eulenberg (*Arch. Pharm.* [2], cxlvii. 130; *Chem. Soc. J.* [2], ix. 1075), snuff contains not more than 0.0392 to 0.062 p.c. nicotine. The strongest tobacco for chewing was found to contain only a trace, and other specimens none at all, so that nothing like nicotine-poisoning can result from the use of such tobacco. Vohl a. Eulenberg also confirm the observations of Zeise, made in 1843, that nicotine is not present in the smoke of tobacco (see *Tobacco*).

Double salts of nicotine with zinc chloride and cadmium chloride have been prepared by H. Vohl (*J. pr. Chem.* [2], ii. 331). The *zinc salt*,  $(\text{C}^4\text{H}^7\text{N.HCl})^2.\text{ZnCl}^2 + 4\text{H}^2\text{O}$ , is obtained by mixing a neutral alcoholic solution of zinc chloride with an alcoholic solution of nicotine, and dissolving the precipitate in hydrochloric acid, avoiding an excess. The salt is then deposited in shining tables or prisms, and may be advantageously recrystallised from boiling alcohol of 80 p.c. It is permanent in the air, easily soluble in water, almost insoluble in absolute alcohol and in ether, smells faintly of nicotine, and has a faint acid reaction. When left over sulphuric acid, or heated to  $100^\circ$ , it gives off all its water of crystallisation; in the latter case also part of its nicotine. The *cadmium salt*,  $(\text{C}^4\text{H}^7\text{N.HCl})^2.\text{CdCl}^2 + 2\text{H}^2\text{O}$ , prepared like the zinc-salt, crystallises in beautiful concentric groups of needles and prisms. It is easily soluble in water and in alcohol of 80 p.c., insoluble in ether; gradually turns brown when exposed to the air.

**NIGELLA SEEDS or BLACK CUMMIN.** The seeds of *Nigella arvensis*, a ranunculaceous plant growing on the Mediterranean coasts, and in Egypt, Trans-Caucasia, and India, were found by Reinsch, in 1841, to yield 35.8 p.c. of fat oil, 0.8 p.c. of volatile oil, and only 0.6 p.c. of ash. He gave the name of *Nigellin* to a bitter extract resembling turpentine, yet soluble in water as well as in alcohol, though not in ether.

By submitting 25 lbs. of fresh seed to distillation, Flückiger (*Pharm. J. Trans.* [2], ii. 161) has obtained a nearly colourless essential oil in even smaller quantity than Reinsch. It has a slight odour, somewhat resembling that of parsley oil, with a magnificent bluish fluorescence, as already remarked by Reinsch. In a column 50 mm. long this oil deviates the ray of polarised light  $9.8^\circ$  to the left. Its specific gravity is 0.8909. The chief part of it, when distilled with chloride of calcium in a current of dry carbonic acid, comes over at  $256^\circ$ . It contains: carbon 83.3, and hydrogen 11.8 p.c., corresponding with the formula  $2C^{10}H^{15}.H^{2}O$ .

The residual portion, which was almost entirely devoid of rotatory power, yielded carbon 87.89, and hydrogen 11.72 p.c., after having been rectified by means of sodium. This part of the oil consequently belongs to the terpenes  $C^{10}H^{16}$ .

The fat oil, extracted by means of boiling ether from seed grown in Germany, previously finely powdered (necessarily including some essential oil which imparted to the other its fluorescence) amounted to 25.6 p.c. It is a fluid fat which does not congeal at  $15^\circ$ ; it was found to consist chiefly of olein, besides which it yielded a considerable amount of a solid fatty acid, the crystals of which, after reiterated purification, melted at  $55^\circ$ . The melting point did not rise by recrystallisation, the acid being probably a mixture of palmitic and myristic acids.

*Nigella* seeds, powdered and dried over sulphuric acid, yielded 3.3195 p.c. of nitrogen, answering to about  $21\frac{1}{2}$  p.c. of albuminous matter.

It is stated in the *Pharmacopœia of India* that *Nigella* seeds are carminative, and they were formerly so regarded in Europe. In the East generally they are used as a condiment to food, and in Greece, Turkey, and Egypt they are frequently strewed over the surface of bread and cakes in the same manner as anise or sesame. The fixed oil of the seeds is also expressed for use.

**NIGHTSHADE.** On the variations in the quantity of atropine in the leaves and root of the Deadly Nightshade in different seasons, see *ATROPA* (p. 117).

**NIIN.** This name is given to the fatty product of an insect found in Yucatan. It is a yellowish-brown fatty mass, which has a neutral reaction, absorbs oxygen from the air, melts at  $48.9^\circ$ , and resolidifies between  $26.7^\circ$  and  $24.9^\circ$ ; dissolves easily in ether, benzene, chloroform, and oil of turpentine, but is insoluble in alcohol; saponifies with difficulty, yielding a pungent-smelling acid called *niic acid*, and a volatile oil, together with palmitic and stearic acids. Ammonia colours it red. Its solution in turpentine-oil is converted, by exposure to the air, into a resinous syrup (A. Schott, *Chem. News*, xxii. 110).

**NIOBUM.** Elaborate investigations of the composition of natural niobates and tantalates have been published by Rammelsberg (see *TANTALATES*).

For R. Hermann's investigations on the compounds of niobium and the supposed element *Umenium*, and the method of separating the two, see *J. pr. Chem.* [2], iii. 373, iv. 178; *Bull. Soc. Chim.* [2], xvi. 256; *Jahresb. f. Chem.* 1871, 287–292.

**NITROCARBOL.** Syn. with NITROMETHANE.

**NITRO-COMPOUNDS OF THE FATTY SERIES.** See NITROPARAFFINS under PARAFFIN.

**NITROGEN.** On the quantivalence of this element, see Sestini (*Cimento*, 1871-72, p. 274; *Chem. Soc. J.* [2], x. 962).

On the constitution of the Pentatomic Compounds of Nitrogen, see Blomstrand (*J. pr. Chem.* [2], iii. 186).

**Preparation.**—Pure nitrogen may be obtained from atmospheric air by introducing into a flask of 10 to 14 litres capacity about 200 grams of copper-turnings free from other metals, and partly covering them with aqueous ammonia, the flask being then closed by a cork fitted with a safety-tube and a gas delivery-tube stopped at the end with a caoutchouc-cap. If the flask be shaken from time to time, the whole of the oxygen, even that which may enter by the safety-tube in consequence of changes of atmospheric pressure, will be completely absorbed in a day or two. The nitrogen gas then be transferred to another vessel by pouring in water previously freed from oxygen by means of copper and ammonia, and washed with strong sulphuric acid (Berthelot *Bull. Soc. Chim.* [2], xiii. 314).

**NITROGEN OXIDES.** Monoxide,  $N_2O$ . T. Willis (*Chem. Soc. J.* [2], xi. 21) has succeeded in solidifying this compound by means of the cold arising from it

own evaporation when in the liquid state, the evaporation being aided by a strong current of air. A very fine steel tube is directed into the axis of a thin brass cone, having a small opening, about the eighth of an inch at its apex. On causing a stream of the liquid to issue from the jet, it is retained in the cone for a moment, and then forcibly blown out at the apex, together with a strong stream of air. The solid is in this way formed in some quantity, and may be collected in a dish lined with filter-paper, or other suitable vessel.

The appearance of the solid is more compact than that of the well-known carbonic snow, probably because larger particles of the liquid are frozen, this freezing taking place with carbonic acid immediately the jet of liquid leaves the tube, and while it is yet in the state of fine spray, but in the case of nitrogen monoxide, only after it has to some extent been collected into larger drops. Unlike solid carbonic acid, nitrogen monoxide will melt and boil, if gently warmed before assuming the gaseous condition. Hence, if touched with the fingers, or placed in contact with the skin, it melts, producing a painful blister. The temperature of its freezing or melting point is  $-120^{\circ}$  F., or  $-99^{\circ}$  C., as observed with an alcohol thermometer. The boiling point, usually said to be  $-88^{\circ}$  C., seems to be really  $-109^{\circ}$  F. or  $-92^{\circ}$  C. The proximity of the boiling and freezing points renders it possible to freeze the liquid by simply blowing a stream of air through it.

The specific gravity of liquid nitrogen monoxide is about 0.9004; it is not miscible with water.

*Salts of Nitrogen Monoxide*, NOM or  $N^{\circ}O.M^{\circ}O$ . *Hyponitrites* (Divers, *Proc. Roy. Soc.* xix, 425).—When a solution of nitrate of sodium or other alkali-metal is mixed with a quantity of sodium-amalgam, more than sufficient to reduce it to nitrite, red vapours are produced with effervescence. If the liquid be then cooled and more of the amalgam added very gradually, the evolution of red vapours recommences briskly after 2 atoms of sodium have been added, and ceases after the addition of 4 atoms of sodium. The liquid then contains, though in comparatively small quantity, a hyponitrite of sodium. The corresponding *silver salt*,  $NOAg$  or  $Ag^{\circ}O.N^{\circ}O$ , is prepared by neutralising with acetic acid, precipitating with silver nitrate, washing the yellow precipitate, and drying at  $100^{\circ}$ . If the precipitate should be black, as sometimes arises from the presence of a body formed from the sodium, rock-oil, and silver acetate, it may be purified by dissolving it, after washing, in very weak nitric acid, filtering carefully, adding ammonia to alkaline reaction, and then adding acetic acid.

The precipitate is stable at temperatures a little above  $100^{\circ}$  and nearly as difficult of solution in water as silver chloride. It is not affected by light, is insoluble in acetic acid, but soluble in ammonia and in dilute sulphuric and nitric acids, and may be separated unaltered from these solutions. Strong nitric acid oxidises it immediately with evolution of red vapours; moderately concentrated acids decompose it, with formation of nitrogen, nitrous acid, and nitric acid. It is also decomposed by soluble chlorides and by hydrogen sulphide.

The original solution of the sodium hyponitrite, mixed with acetic acid till silver nitrate no longer forms with it a brown precipitate, gives insoluble precipitates with most metals. With potassium iodide it gives no sensible reaction, but a solution containing free iodine is immediately decolorised by it, both in neutral and in acid solution. Heated with acetic acid it gives off nitrogen monoxide:



*Trioxide or Nitrous Anhydride*,  $N^{\circ}O^{\circ}$ . This oxide is formed by the direct combination of nitrogen dioxide and oxygen in the proportion by volume of 4 : 1 ( $= N^{\circ}O^{\circ} : O$ ), also by the combination of the dioxide and tetroxide when the two gases in equal volumes ( $NO : NO^{\circ}$ ) are passed through a red-hot tube. The latter is indeed a very convenient method of preparing the pure trioxide, which, as thus obtained, is a liquid having at ordinary temperatures a dark blue colour, changing at  $-10^{\circ}$  to a splendid indigo-blue; it does not solidify at  $-30^{\circ}$  (Hasenbach, *J. pr. Chem.* [2], iv, 1).

Nitrogen trioxide may also be prepared by decomposing the so-called lead-chamber crystals with water. To prepare a concentrated solution of these crystals, dry sulphurous anhydride is passed into well-cooled fuming nitric acid, till the liquid becomes oily and evolves much gas on the addition of water. This solution is placed in a flask provided with a double-bored cork, dropping funnel, &c., and the current of gas is regulated by the quantity of water added (H. Streiff, *Deut. Chem. Ges. Ber.* v, 285).

*Reactions.*—1. The reaction of nitrous anhydride with water varies according to the proportion in which the two are mixed. With a relatively small quantity of water, nitrous anhydride, or the compound  $2SO^{\circ}.N^{\circ}O^{\circ}.H^{\circ}O$ , gives nitric acid and absolutely pure nitrogen dioxide. In a large excess of cold water, on the other hand, nitrous

anhydride dissolves without decomposition. The solution thus formed may be kept unaltered for several days, and when boiled gives off, though not immediately, tri- and dioxide of nitrogen. 2. When indifferent pulverulent bodies, such as sand, gypsum, and especially charcoal, are introduced into the solution of nitrous acid, it is immediately decomposed into nitric acid and nitrogen dioxide. Nitrous acid is a strong reducing agent, and acts in this manner on auric chlorido and potassium permanganate. 3. *Sulphurous acid* forms with nitrous acid at ordinary temperatures several nitrosulphuric acids; when heated it yields the products of decomposition of these acids—viz., nitrogen dioxide, ammoniac, and even nitrogen monoxide. The action of sulphurous acid on the compound of nitrous acid and sulphuric acid gives rise to the evolution of a large quantity of nitrogen dioxide. When the mixed solution of sulphurous and nitrous acid is warmed, nitrogen monoxide is evolved, wherein, according to Frémy, may perhaps be found the cause of the great loss of nitric acid which takes place in the manufacture of sulphuric acid; in fact, nitric acid when heated with sulphurous acid likewise gives off nitrogen monoxide. By many reducing agents, nitrous acid, nitric acid, and their salts are reduced, with formation of ammoniac and a small quantity of hydroxylamine,  $\text{NH}_2\text{O}$  (Frémy, *Compt. rend.* lxx. 61).

**Detection and Estimation of Nitrous Acid.**—The following modes of detection are given by Chataud (*Chem. News*, xxiv. 225). 1. The liquid to be tested for nitrous acid is mixed with *potassium ferrocyanide* and *acetic acid* and boiled, then left to cool and treated with ammonium sulphide; if nitrous acid is present the liquid turns blue. 2. The liquid to be tested is evaporated nearly to dryness and the residue triturated with two drops of solution of *aniline sulphate*, whereupon, if nitrous acid is present, a distinct odour of phenol is omitted. This reaction is regarded by Chataud as the most delicate of all tests for nitrous acid; moreover it affords a certain distinction between nitrous and nitric acid, which latter gives with aniline only a yellow coloration, but no odour of phenol.

3. For the detection of nitrous acid in spring, rain, and river water, P. Griess (*Ann. Chim. Phys.* cliv. 333) uses a solution of *diamidobenzoic sulphate* (iv. 294), which, with a large quantity of nitrous acid, produces a brown-red amorphous precipitate; with a small quantity, a more or less strong yellow coloration. This reaction is capable of indicating the presence of 1 pt. nitrous acid in 5,000,000 parts of water, i.e. of  $\frac{1}{5}$  milligram in a litre. For quantitative estimation an aqueous solution of nitrous acid of known strength is added to a solution of diamidobenzoic acid till a shade of colour is produced identical with that which is developed by the same solution in the liquid under examination. For this estimation the following liquids are required: (1). A solution of diamidobenzoic sulphate saturated in the cold; if coloured it must, before use, be treated with animal charcoal. (2). A normal solution of silver nitrite prepared by dissolving 0.328 gram of the salt in a litre of water; each cubic centimeter of this solution is equivalent to  $\frac{1}{10}$  milligram nitrous acid. (3). Colourless sulphuric acid free from nitric acid. (4). Perfectly colourless distilled water.

The water to be examined must, if coloured, be decolorised by addition of a few drops of aluminium sulphate solution, and subsequent addition of sodium carbonate; the precipitate thereby formed does not carry nitrous acid down with it. After the water thus decolorised has been passed through a filter previously freed from adhering nitrous acid by washing with water containing sulphuric acid, a tall glass cylinder about an inch in diameter is filled with it to a mark of 100 c.c., about  $\frac{1}{2}$  c.c. solution of diamidobenzoic acid solution is added, together with a few drops of sulphuric acid, and the liquid is left at rest for about a quarter of an hour, by which time the colour is fully developed. A second cylinder of the same diameter is then filled to the mark of 100 c.c. with distilled water, diamidobenzoic and sulphuric acid added as before, and then a quantity of the normal solution of silver nitrite sufficient to produce the same depth of colour as in the first cylinder. The colours of the two liquids must be compared together after a quarter of an hour, best near a window. The quantity of the normal solution of nitrous acid used gives directly the amount of nitrous acid in the water under examination.

Respecting the estimation of nitrous acid in nitrous sulphuric acid, see G. E. Davies (*Chem. News*, xxiv. 257, xxv. 25; *Chem. Soc. J.* [2], x. 173), and W. Crowder (*Chem. News*, xxiv. 237 and 240; *Chem. Soc. J.* [2], x. 174).

**Nitrites.** *Ammonium nitrite*.—On the simultaneous formation of ammonium nitrite, hydrogen dioxide, and ozone, in the combustion of hydrogen in the air, see HYDROGEN (p. 660).

*Cobalt nitrites* (S. P. Sadtler, *Sill. Am. J.* [2], xlix. 189).—Erdmann found that when cobalt salts are precipitated by potassium nitrite, various products are formed accordingly as the cobalt solution is acid or neutral, and that the 'neutral salt',  $3\text{CoK}^+(\text{NO}_2)^+ + \text{H}_2\text{O}$ , is likewise formed in an atmosphere of carbon dioxide (*J. pr. Chem.* xlvii. 385). The salt examined by Sadtler was prepared by mixing a solution

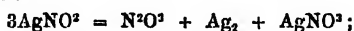
of cobalt chloride, strongly acidulated with acetic acid, with a concentrated solution of potassium nitrite. This salt, after washing with potassium acetate and then with alcohol, has the composition of tripotassio-cobaltic nitrite,  $\text{Co}^2\text{O}^3 \cdot 3\text{N}^2\text{O}^3 + 3(\text{K}^2\text{O} \cdot \text{N}^2\text{O}^3)$ , or  $\text{Co}^2(\text{NO}^2)^3 \cdot 6\text{KNO}^2$ . According to the concentration of the solutions employed, it contains 4, 3, 2, 1 mol.  $\text{H}^2\text{O}$ , or is anhydrous, the colour varying at the same time from light yellow to dark greenish-yellow. Hence it appears that mixtures of salts containing different amounts of crystallisation-water are very apt to form, so that it is difficult to give a definite process for the preparation of either of them.

When a solution of cobalt chloride, kept constantly acid with acetic acid, is mixed with sodium nitrite, brown disodiocobaltic nitrite,  $\text{Co}^2(\text{NO}^2)^3 \cdot 4\text{NaNO}^2 + \text{H}^2\text{O}$ , is precipitated, and on further addition of sodium nitrite, yellow trisodiocobaltic nitrite,  $\text{Co}^2(\text{NO}^2)^3 \cdot 6\text{NaNO}^2 + \text{H}^2\text{O}$ . The solution of the latter salt yields, on addition of luteo-cobaltic chloride, a crystalline yellow salt, in which the sodium is replaced by luteo-cobalt, giving the formula  $\text{Co}^2(\text{NO}^2)^3 + \text{Co}^2 \cdot 12\text{NH}^3(\text{NO}^2)^3 + \text{H}^2\text{O}$ . In like manner are obtained the corresponding roseo-cobaltic salt,  $\text{Co}^2(\text{NO}^2)^3 + \text{Co}^2 \cdot 10(\text{NH}^3 \cdot \text{NO}^2)^3 + \text{H}^2\text{O}$ , and a xantho-cobaltic salt not yet analysed. The ammonium salts corresponding with the sodium salts, viz. diammonio-cobaltic nitrite,  $\text{Co}^2(\text{NO}^2)^3 \cdot 4(\text{NH}^3 \cdot \text{NO}^2) + 2\text{H}^2\text{O}$ , and triammonio-cobaltic nitrite,  $\text{Co}^2(\text{NO}^2)^3 \cdot 6(\text{NH}^3 \cdot \text{NO}^2) + 2\text{H}^2\text{O}$ , have also been prepared; but the conditions of their formation have not been determined further than that the formation of the triammonium salt is favoured by the use of concentrated solutions.

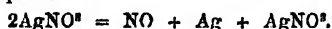
The addition of potassium nitrite to a warm dilute neutral solution of cobaltous chloride produces first a black or green precipitate of potassio-dicobaltous nitrite,  $2\text{Co}(\text{NO}^2)^2 \cdot 2\text{KNO}^2 + \text{H}^2\text{O}$ , and afterwards a yellow slightly crystalline or amorphous precipitate of potassio-monocobaltous nitrite,  $\text{Co}(\text{NO}^2)^2 \cdot 2\text{KNO}^2 + \text{H}^2\text{O}$ .

Respecting the Nitrites of Platinum-bases, see PLATINUM-BASES, AMMONIACAL.

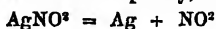
*Silver nitrite*,  $\text{AgNO}^2$ , heated in an open crucible or a watch-glass, is decomposed according to the equation—



in a well-covered crucible, on the contrary, the decomposition takes place in the manner represented by the equation—

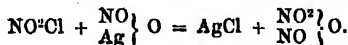


And, lastly, when the salt is heated for a long time to  $98^\circ$ – $140^\circ$  in dry air, or in aqueous vapour, it is decomposed almost completely, according to the equation—



(Divers, *Chem. Soc. J.* [2], ix. 85).

**Tetroxide**,  $\text{NO}^2$  or  $\text{N}^2\text{O}^4$ . This oxide is produced by the action of nitryl chloride on silver nitrite:



This reaction tends to the conclusion that the rational formula of the tetroxide is  $\text{NO}^2 \} \text{O}$  (A. Exner, *Chem. Centr.* 1872, 273).

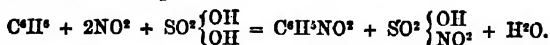
Nitrogen tetroxide is also formed by the direct combination of oxygen with the trioxide, which is easily effected by passing a stream of oxygen or air into the mixture of nitrogen trioxide and tetroxide evolved by the action of fuming nitric acid on arsenious acid. The liquid tetroxide thus obtained is pure enough for most purposes after one rectification (Hasenbach, *J. pr. Chem.* [2]. iv. 1).

**Reactions.**—1. Nitrogen tetroxide unites at high temperatures with the *dioxide*, producing the trioxide:  $\text{NO}^2 + \text{NO} = \text{N}^2\text{O}^3$  (p. 853). This seems to show that the molecule of the tetroxide at ordinary temperatures contains  $\text{N}^2\text{O}^4$ , and that it is split up at high temperatures into 2 molecules of  $\text{NO}^2$ . At comparatively low temperatures the affinity of the dioxide for the group  $\text{NO}^2$  does not appear to be strong enough to split up the molecule  $\text{N}^2\text{O}^4$ ; but as soon as this separation is effected by the action of heat, the  $\text{NO}^2$  thus set free unites with  $\text{NO}$ , producing  $\text{N}^2\text{O}^3$ .

In like manner, the combination of  $\text{NO}^2$  with  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{Cy}$ , may be effected by the action of chlorine, &c. on the heated tetroxide. Nitryl chloride,  $\text{NO}^2\text{Cl}$ , is easily obtained in this manner. The bromide is formed in like manner, but is partly resolved into its constituents by distillation; the iodide is not formed by the action of iodine on the heated tetroxide. By passing cyanogen and nitrogen tetroxide through a red-hot tube, white silky needles are obtained, which explode with fearful violence without any assignable cause, even at low temperatures; in consequence of this, their composition could not be determined, but they probably consist of nitryl cyanide,  $\text{NO}^2\text{Cy}$ .

Nitrogen tetroxide acts on *sulphuric anhydride*, forming the compound  $\text{N}^2\text{O}^5\text{SO}^4$ .

With *sulphurous anhydride*, nitrogen tetroxide unites to a white solid mass, probably having the composition  $\text{SO}^2(\text{NO}^2)^2$ . *Carbon monoxide* is partly oxidised by nitrogen tetroxide at ordinary temperatures, and partly combines with it, forming a very volatile liquid, which is decomposed, with effervescence, by water. *Benzene* is acted upon by nitrogen tetroxide, yielding nitrobenzene and oxalic acid. When sulphuric acid is added to a mixture of benzene and nitrogen tetroxide, nitrobenzene is formed, probably according to the equation—



**Pentoxide. Nitric Anhydride,  $\text{N}^2\text{O}^5$ .** *Preparation.*—R. Weber (*Pogg. Ann.* cxlvii. 113) prepares this compound by the action of phosphoric anhydride on nitric acid. The strongest nitric acid, freed as completely as possible from nitrous acid and cooled by ice, is treated with phosphoric anhydride added slowly and by small quantities at a time. The syrupy liquid is distilled as long as anything comes over at a blood-heat, and condenses in oily drops in the neck of the retort; and the two layers of the distillate are separated by decantation, the lower consisting mainly of nitric hemihydrate,  $2\text{N}^2\text{O}^5 \cdot \text{H}^2\text{O}$ . The upper layer, which consists of nitric anhydride, nitrous acid, and some of the hydrate, is cooled by ice-water, which renders it turbid, and causes a small quantity of a clear coloured liquid to separate. This liquid, which consists of nitric anhydride and nitrous acid, is further cooled by ice or a freezing-mixture, when some of the nitric anhydride crystallises in well-formed, transparent, yellowish prisms, leaving a liquid compound of nitric anhydride and nitrous acid, which appears to be richer in the former than nitroso-nitric acid. Lastly, the anhydride is purified by cautiously fusing it, again crystallising it by cold, and draining off the mother-liquor.

Berthelot (*J. Pharm.* [4], xix. 182) cools the nitric acid by a freezing-mixture, so as to prevent the temperature from rising above zero, and after all the phosphoric anhydride has been added, transfers the pasty mass quickly to a tubulated retort capable of containing five or six times the quantity, and distils very slowly, collecting the product in stoppered bottles surrounded with ice.

Nitric anhydride melts at about  $30^\circ$ ; its specific gravity in the solid state is above 1.64, in the liquid state less than 1.636.

It is very unstable, particularly in the fused state, but can be preserved for several days at  $10^\circ$  in a dry atmosphere. It is volatile at ordinary temperatures, and its vapour condenses in beautiful crystals in the cooler part of the tube containing it. In a freezing mixture it is almost colourless (Weber).

It is not explosive either in the solid or in the gaseous state, but as it gradually decomposes even at ordinary temperatures into oxygen and the tetroxide, it should be preserved in stoppered bottles, not in sealed tubes (Berthelot).

Nitric anhydride acts with great violence on sulphur, forming a compound of sulphuric anhydride and nitrous acid. It also acts with great energy on phosphorus, potassium, and sodium, setting them on fire. Upon organic substances it also acts with great intensity. It does not act upon charcoal, but this substance when previously kindled burns with great brilliancy in its vapour. It acts on zinc, cadmium, mercury, and arsenic, and slightly on magnesium and thallium, but has no action on most other metals (Weber).

**Nitric Hemihydrate,  $2\text{N}^2\text{O}^5 \cdot \text{H}^2\text{O}$ .** This hydrate crystallises out on cooling the lower layer of the distillate from nitric acid and phosphoric anhydride in a freezing mixture. It can also be prepared by adding nitric anhydride to nitric acid. The anhydride dissolves, with development of heat, until the hemihydrate is produced, but any further quantity of it remains insoluble. The pure hemihydrate is obtained by crystallising it out in a freezing-mixture, draining it from the mother-liquor, allowing it to melt, and again crystallising it. In its chemical properties the hydrate resembles the anhydride. It is liquid at ordinary temperatures, but less so than the ordinary monohydrate, and more or less yellow-coloured; solid at about  $-5^\circ$ . Its specific gravity at  $18^\circ$  is 1.642. It decomposes slowly at ordinary temperatures. When heated it partly distils unchanged, but nitric anhydride is also formed, so that the distillate consists of two layers, the upper being the anhydride. In this decomposition it resembles fuming sulphuric acid (Weber).

**Nitric Monohydrate, Nitric Acid,  $\text{N}^2\text{O}^5 \cdot \text{H}^2\text{O}$  or  $\text{NO}^2\text{H}$ .** *Occurrence.*—Goppelsröder (*Zeitschr. anal. Chem.* x. 259, xi. 16) has determined the quantities of nitric acid and ammonium nitrate in rain-water and snow (at Basel), for the twelve months from October 1870 to September 1871. The results are given in the following table:—



Months 1870-71	Total amount of rain and snow-water	Minimum		Maximum	
		Amount contained in 1,000,000 parts of the collected rain or snow-water			
		N <sup>o</sup> O <sup>s</sup>	NH <sup>4</sup> .NO <sup>s</sup>	N <sup>o</sup> O <sup>s</sup>	NH <sup>4</sup> .NO <sup>s</sup>
October, 1870 .	101.2 mm.	trace	trace	13.6	20.1
November " .	123.9 "	.5	.7	1.2	1.8
December " .	91.2 "	.4	.6	5.3	7.8
January, 1871 .	37.4 "	3.1	4.6	6.3	7.8
February " .	38.5 "	2.2	3.2	4.4	6.5
March " .	27.5 "	2.6	3.8	12.3	18.2
April " .	107.4 "	2.2	3.2	4.6	6.8
May " .	41.3 "	2.2	3.2	10.	14.8
June " .	114.5 "	2.3	3.2	6.2	9.1
July " .	141.4 "	6.41	0.6	1.1	0.63
August " .	26.9 "	0.08	0.11	0.98	1.4
September " .	41.6 "	0.6	0.87	1.0	1.46

Former observers, among whom are Barral, Bobierre, Boussingault, Bineau, and Knop, found from 0.1 to 16 parts of nitric acid in a million parts of atmospheric deposit.

According to Chabrier (*Compt. rend.*) rain-water which falls when the air is tranquil contains more nitrous than nitric acid, but in storms the nitric acid predominates, especially if the rain is collected in the middle of the storm.

C. Ekin (*Chem. Soc. J.* [2], ix. 64) found in the spring-water of an uncultivated hill near Bath, not exposed to any contamination with organic matters, 65 grains of nitric acid in a gallon. The rocks and fossils of this hill were found to contain the following proportions of nitrogen in a million parts.

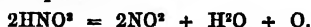
Grey chalk marl . . . . .	1.1
Bath oolite . . . . .	1.3
Fossils from the green-sand . . . . .	2.23
" " lias . . . . .	3.6 to 4
" " Fuller's-earth . . . . .	3.0
Inferior oolite . . . . .	6.9 to 7.6

**Formation.**—When hydrogen is burnt in oxygen in a large flask to which air is at the same time admitted, the flask becomes filled with red vapours, and the water which condenses contains a considerable quantity of nitric acid (Hofmann, *Deut. Chem. Ges. Ber.* iii. 658).

**Decomposition by Heat.**—It is well known that nitric acid is decomposed by heat into oxygen, water, and nitrogen tetroxide, the decomposition beginning at the boiling point of the acid and being complete at a red heat. To ascertain with greater accuracy the nature of the products, the gradual increase of the decomposition with the temperature, and the point at which it becomes complete, Carius (*Deut. Chem. Ges. Ber.* iv. 828) has made the following determinations of the specific gravities of the gas produced at different temperatures.

Temperature of the decomposition	Specific gravity of the Mixed Gases		
	Air = 1	Difference	H = 1
0			
86	2.05	—	29.6
100	2.02	—	29.1
130	1.92	0.10	27.6
160	1.79	0.13	25.8
190	1.59	0.20	23.0
220	1.42	0.17	20.4
250	1.29	0.13	18.6
256	1.25	—	17.9
265	1.24	—	17.8
312	1.23	—	—

These numbers show that the specific gravity of the gases produced by the decomposition of nitric acid remains constant from about  $256^{\circ}$  to  $312^{\circ}$ , whence also it appears that from  $256^{\circ}$  upwards no further change takes place in the composition of these gases. Moreover their specific gravity, which is nearly 18 ( $H = 1$ ), is  $\frac{4}{5}$  of 31.5 the sp. gr. of nitric acid vapour, which is just what it should be if the decomposition takes place as shown by the equation:



The result negatives the supposition—improbable also for other reasons—that the vapours contain nitrous acid.

To ascertain approximately the quantities of oxygen set free at different temperatures, nitric acid enclosed together with air in a sealed tube was heated, and the increase of volume of the air on opening the tube under water was measured; this gave the volume of the oxygen set free by the decomposition. The results are given in the following table:—

1 gram of Nitric acid yields of Oxygen gas:—

	In presence of air:			
	15 c.c.	250 c.c.	1200 c.c.	Calculated
°	c.c.	c.c.	c.c.	c.c.
130	13.08	15.47	16.89	17.26
180	22.70	33.30	38.45	37.26
200	23.39	—	50.80	52.05

The quantity of oxygen increases up to a certain point with the quantity of air present and the temperature of decomposition; above  $200^{\circ}$  there were found, for equal quantities of air added, nearly equal quantities of oxygen. Lastly, on calculating the quantities of oxygen set free, from the specific gravities of the mixed vapours, these quantities below  $200^{\circ}$  are found to be nearly equal to those obtained in presence of large quantities of air.

The specific gravities of the mixed vapours afford the means of calculating the amounts per cent. of nitric acid decomposed, according to the preceding equation, at different temperatures below  $256^{\circ}$ , and the quantities of oxygen thereby formed. The results are as follows:—

Temperature of decomposition	Sp. gr. $H = 1$	Decomposition per cent.	Oxygen from 1 gram $\text{HNO}_3$
°			c.c.
86	20.6	9.53	8.43
100	29.1	11.77	10.41
130	27.6	18.78	16.62
160	25.8	28.96	26.22
190	23.0	49.34	43.69
220	20.4	72.07	63.77
250	18.6	93.03	82.30
256	18.0	100.00	88.47

On the Electrolysis of Nitric Acid, see Bourgoin (*Compt. rend.* lxx. 811; *J. Pharm. Chim.* [4], xii. 110, xiii. 266; *Chem. Soc. J.* [2], ix. 886).

**Estimation.**—For the estimation of nitric acid in well-water, Marx in 1868 proposed a volumetric method based on the decoloration of indigo by nitric acid. The water is mixed with twice its volume of strong sulphuric acid, whereby its temperature is raised to about  $120^{\circ}$ , and a standard solution of indigo (4 c.c. = 1 mgrm. nitric acid) is poured into it till a distinct green colour is produced (*Zeitschr. anal. Chem.* vii. 412). Several modifications of this method, with the view of rendering it more accurate, have been proposed by Goppelsröder (*ibid.* ix. 1), Trommsdorff (*ibid.* ix. 167), Bemmelen (*ibid.* xi. 186; *Chem. Soc. J.* [2], xi. 90), and F. Fischer (*J. pr. Chem.* [2], vii. 57; *Chem. Soc. J.* [2], xi. 1054).

An apparatus for the performance of Schlösing's method of estimating nitric acid

based on the reducing action of boiling hydrochloric acid and ferrous chloride on nitrates (iv. 88), together with certain modifications in the method, is described by E. Reichardt (*Zeitschr. anal. Chem.* ix. 24; *Chem. Soc. J.* [2], ix. 439). Another modification of the method is described by E. Fleischer (*Zeitschr. anal. Chem.* xi. 309; *Chem. Soc. J.* [2], xi. 529).

For the estimation of nitric acid in saltpetre, A. Wagner (*Dingl. pol. J.* cc. 120, cci. 423; *Chem. Soc. J.* [2], ix. 753, x. 323) makes use of the oxidising action of nitric acid on chromic oxide:



0.3 to 0.4 gram of the saltpetre is heated with 3 grams of chromic oxide and 1 gram of sodium carbonate in a tube from which the air has been previously expelled by a stream of carbon dioxide, which is also slowly kept up during the ignition to expel the nitrogen dioxide evolved. After cooling, the contents of the tube are dissolved in water, the chromic acid precipitated by mercurous nitrate, the precipitate washed with a dilute solution of the same salt, then ignited, and the resulting chromic oxide weighed. 1 part of  $\text{CrO}^3$  is equivalent to 0.7068  $\text{N}^2\text{O}^5$ .

The estimation may also be made by collecting the evolved nitrogen dioxide over mercury in a tube containing oxygen gas and a standard solution of caustic soda, whereby the nitrogen dioxide is converted into nitric acid, which combines with the soda. When no more oxygen is absorbed on shaking the tube, an aliquot part of the soda-solution is titrated back with standard sulphuric acid.

The presence of organic matter vitiates the results of this method. In applying it to the estimation of nitrates in potable waters, Wagner first evaporates the water with sodium carbonate and potassium permanganate.

A method of estimating nitric acid in potable waters, based on Schulze's method of reduction with aluminium, and titration of the ammonia thereby produced, is given by T. P. Blunt (*Chem. News*, xxv. 205; *Chem. Soc. J.* [2], x. 922).

**Metallic Nitrates.** On the Heat of Formation of Nitrates, see HEAT (p. 626).

*Aluminium nitrate*, prepared by dissolving recently precipitated alumina in dilute nitric acid, crystallises in rhombic pyramids truncated by horizontal prisms, dissolves easily in water and alcohol, is very hygroscopic, and has a strong acid reaction (E. Thorey, *Russ. Zeitschr. Pharm.* x. 321).

*Ammonium nitrate*.—This salt is capable of condensing considerable quantities of ammonia gas, forming a liquid the properties of which have been studied by E. Divers (*Proc. Roy. Soc.* xxi. 107).

*Ammoniated ammonium nitrate* varies in composition according to the temperature and pressure. At a temperature of  $23^\circ$  and the pressure of the atmosphere, it consists of about 4 parts of nitrate to one of ammonia by weight; but under greater pressure or at lower temperatures, much more ammonia can be condensed by the nitrate. At  $0^\circ$  and the pressure of the atmosphere, 2 parts of nitrate can condense 1 part of ammonia. Like an aqueous solution, the liquid boils when heated, and, when nearly saturated with the nitrate, deposits crystals of it when cooled. It can also, like an aqueous solution, be heated above its boiling point without boiling, and become supersaturated with the salt without crystallising. During its decomposition cold is manifested, and during its formation heat is evolved, but not to a great extent, because the heat given out by the liquefaction of the ammonia is nearly all used up in the liquefaction of the nitrate.

The specific gravity of the liquid varies with its composition. When it consists of two of nitrate to one of ammonia, it has a specific gravity of 1.0725; when it consists of four of nitrate to one of ammonia, it has a specific gravity of nearly 1.200. Its specific gravity can be calculated from its composition by taking 1.5245 as the specific gravity of the nitrate, and 0.671 as that of the ammonia.

In its rate of expansion by heat, the liquid resembles others which exist as such at ordinary temperatures, rather than those which, like ammonia itself, are retained as such only by great pressure. Its expansivity increases with the quantity of ammonia present.

Its action upon a great number of substances, principally inorganic, resembles for the most part the actions of dry ammonia and ammonia nitrate conjoined. The nitrate appears to undergo double decomposition with most salts, and the ammonia to unite with nearly all, including the salts of magnesium, aluminium, iron, and manganese. The ammoniated compounds which do not dissolve in the liquid are very bulky. Nitrates, chlorides, iodides, and bromides, are either soluble or are decomposed into soluble chlorides, &c., of ammonium, and insoluble ammoniated compounds of the metals. Sulphates, oxalates, chromates, and arsenites are insoluble, and phosphates are nearly so. Phosphoric and chromic anhydrides do not act upon the liquid with

the energy that might be expected, but combine with the ammonia. Iodine dissolves freely. Bromine generates nitrogen. Lead salts, including sulphate, chloride, iodide, and oxide, are freely soluble as ammoniated compounds. Platinous chloride dissolves freely as tetrammonio-platinous chloride. Potassium salts are very sparingly soluble. Alkalis and their carbonates decompose the nitrate; so do litharge, lime, and baryta. Calomel is converted into metallic mercury and a soluble ammoniated mercuric compound. Potassium, sodium, zinc, and cadmium dissolve without liberating gas, by reducing the nitrate to nitrite, potassium taking fire. Magnesium slowly dissolves, liberating a little hydrogen, reducing the nitrate, and becoming partly converted into Beetz's black suboxide of magnesium. Methyl iodide is decomposed; butyric ether and chloroform dissolve sparingly without decomposition. Ether is insoluble, but by its contact causes the liquid to break up into its two constituents.

Ammoniated ammonia nitrate is a good electrolyte, ammonia and hydrogen appearing at the negative electrode, and nitrogen and ammonia nitrate at the positive electrode. Positive electrodes of silver, lead, copper, zinc, and magnesium, are dissolved by the liquid as (ammoniated) nitrates. A positive electrode of mercury is converted into a compound almost insoluble in the liquid. When the electrode is acted upon, the generation of nitrogen does not take place.

*Cerium nitrates* (p. 274).

*Manganous nitrate*.—According to Schulz-Sellack, the solution of this salt in strong nitric acid evaporates to a thin syrup, which deposits crystals consisting of the hydrate  $\text{Mn}^{2+}\text{O}^{2-}\cdot 3\text{H}^2\text{O}$ , that is to say, with half the quantity of water of the ordinary salt (iv. 95).

*Silver nitrate*,  $\text{AgNO}^3$ .—On the action of Hydrogen on this salt, see HYDROGEN (p. 660).

The compounds of silver nitrate with *silver iodide* (iv. 105) have been further examined by C. Stürenberg (*Arch. Pharm.* [2], cxliii. 12). When silver iodide is dissolved in a boiling moderately concentrated solution of the nitrate, the salt,  $2\text{AgNO}^3$ .AgI, crystallises out on cooling; but on saturating the solution completely with silver iodide, another double salt is obtained to which Stürenberg assigns the formula  $2\text{AgNO}^3\cdot 2\text{AgI}$ . When this latter is treated with a concentrated solution of silver nitrate, it dissolves and is converted into  $2\text{AgNO}^3$ .AgI. This salt can be obtained as a finely crystalline precipitate by treating its solution with alcohol. When the salt  $2\text{AgNO}^3\cdot 2\text{AgI}$  is treated with water, silver iodide separates out, but redissolves partly on boiling, the salt  $2\text{AgNO}^3$ .AgI being thereby produced.

When a boiling solution of silver nitrate is incompletely saturated with *lead iodide*, the hot-filtered solution deposits, on cooling, the salt  $8\text{AgNO}^3\cdot 4\text{AgI}\cdot \text{Pb}(\text{NO}^3)^2$  in well-defined colourless prisms belonging to the quadratic system, with the faces  $\infty\text{P}$  and  $\text{P}$ . It is decomposed by water into silver iodide and the nitrates of silver and lead. By prolonged boiling with lead iodide it is converted into the salt  $4\text{AgNO}^3\cdot 4\text{AgI}\cdot 2\text{Pb}(\text{NO}^3)^2$ , which, however, cannot be obtained pure in this manner. It may be prepared in the pure state by mixing the solution containing the two salts with alcohol, whereupon the salt containing the smaller proportion of lead is precipitated, while that which contains the larger proportion crystallises from the liquid in beautiful well-defined hexagonal prisms with the faces  $\infty\text{P}$  and  $\text{P}$ . This salt is decomposed by silver nitrate with formation of  $2\text{AgNO}^3$ .AgI.

*Silver-lead nitrate*,  $2\text{AgNO}^3\cdot \text{Pb}(\text{NO}^3)^2$ , is obtained by evaporating a solution of the mixed nitrates to the crystallising point. The crystals belong to the hexagonal system.

Similar double salts of silver nitrate with mercuric nitrate appear to exist. An experiment similar to those by which the lead salts above described were prepared led to the formation of the salt  $32\text{AgNO}^3\cdot 16\text{AgI}\cdot \text{Hg}(\text{NO}^3)^2$ .

*Uranium nitrate*.—According to Schulz-Sellack (*Zeitschr. f. Chem.* [2], vi. 646) a solution of uranic nitrate, evaporated with a large excess of nitric acid, deposits, on cooling, beautifully fluorescent needles of the salt  $(\text{UO}^2)(\text{NO}^3)^2\cdot 3\text{H}^2\text{O}$  [ $\text{U}^{6+} = 240$ ], whereas, according to Drenckmann (*Jahresb.* 1861, 256), the ordinary salt  $(\text{UO}^2)(\text{NO}^3)^2\cdot 6\text{H}^2\text{O}$  crystallises from acid as well as from neutral solutions. Good crystals of the hydrate  $(\text{UO}^2)(\text{NO}^3)^2\cdot 3\text{H}^2\text{O}$  are obtained by evaporating the acid solution over sulphuric acid and potash; they do not effloresce in a vacuum, but deliquesce in the air, and melt at  $120^\circ$ , whereas the ordinary hydrate melts, according to Ordway, at  $59^\circ$ . According to Pelliot the ordinary hydrate gives off half its water in a vacuum (v. 107), leaving therefore a mass having the composition of the tri-hydrate.

*Yttrium nitrate*,  $\text{Y}(\text{NO}^3)^3\cdot 4\text{H}^2\text{O}$ , forms large colourless crystals easily soluble in water, alcohol, and ether. It is unalterable in the air, but gives off 2 mols. of water when dried at  $100^\circ$  (P. T. Cleve, *Bull. Soc. Chim.* [2], xx. 193).

**Nitric Ethers.** According to P. Champion (*Compt. rend.* lxxiii. 571, 578) the

nitrites of *ethyl*, *amyl*, *hexyl*, and *cetyl*, may be obtained by treating the corresponding alcohols with a mixture of nitric and sulphuric acid.

*Cetyl nitrate*,  $C^{18}H^{35}NO^2$ , prepared by adding pulverised cetyl alcohol to the mixed acids, washing the separated oil with water (best after solution in ether), and drying in a vacuum, is a colourless liquid solidifying between  $12^\circ$  and  $10^\circ$ , and crystallising by slow cooling in long flattened needles. It is slightly soluble in cold alcohol, more soluble in warm alcohol, still more in ether, chloroform, and carbon sulphide, slightly soluble in amyl alcohol and methyl alcohol. Sp. gr. = 0.91. It is decomposed by heat, with separation of charcoal, burns with difficulty, assumes the spheroidal condition when poured upon a hot plate, and then burns with a smoky flame. It is decomposed by strong sulphuric acid.

**NITROGLYCERIN.** On the heat developed in the formation of this compound, see HEAT (p. 626).

On the Explosive force of Nitroglycerin, see EXPLOSION (p. 498).

**NITROMANNITAN.** See MANNITE (p. 775).

**NITROMETHANE**,  $CH^3NO^2$ . See NITROPARAFFINS, under PARAFFINS.

**NITROMETHYLBENZOPHENONE**,  $C^{11}H^{11}(NO^2)O = C^6H^5NO^2 - CO - C^5H^5 - CH^3$ . A body formed by the action of nitric acid of sp. gr. 1.4 on benzyl-toluene at the heat of the water-bath. It crystallises from hot dilute alcohol in long flat needles or silky plates melting at  $127^\circ$  and subliming without decomposition in shining plates. When treated with tin and hydrochloric acid, it yields an amido-compound, forming amorphous salts, from which it is precipitated by soda-solution as a light white powder (Zincke, *Deut. Chem. Ges. Ber.* v. 683).

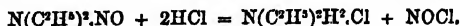
**NITROPROPANE**,  $C^3H^7NO^2$ . See NITROPARAFFINS, under PARAFFINS.

**NITROSODIETHYLAMINE**,  $C^4H^{10}N^2O = N \begin{Bmatrix} C^2H^5 \\ C^2H^5 \\ NO \end{Bmatrix}$ . *Nitrosodiethylin*,

*Nitrosoethylin*.—This compound, formed by the action of potassium nitrite on diethylamine hydrochloride (iv. 114), is somewhat strongly acted upon by potash, soda, and other alkaline bases, either in aqueous or in alcoholic solution; when it is heated therewith in sealed tubes to  $155^\circ$  for about eight hours, the chief products are ammonia and ethylamine. With sodium amalgam, in presence of water, it yields diethylamine and nitrogen monoxide:



Dry hydrogen chloride transforms nitrosodiethylamine into a mass of crystals consisting of diethylammonium chloride, nitrosyl chloride being formed at the same time:



(Gauthier, *Jenaische Zeitschrift*. vii. 118).

**NITRYL CHLORIDE, BROMIDE, IODIDE, and CYANIDE**,  $NO^2Cl$ , &c. On the formation of these compounds by the action of chlorine, &c., on nitrogen tetroxide, see p. 855.

**NOCTILUCIN.** This name is given by T. L. Phipson (*Chem. News*, xxvi. 130) to the peculiar organic substance which causes the production of light in phosphorescent fish, the glow-worm, and probably all other phosphorescent animals; it appears also to be formed, under a variety of circumstances, at the expense of dead animals and vegetable tissue, and even by certain living plants (*Euphorbia*, *Agaricus*, &c.)

Animal noctilucin at the ordinary summer temperature is a semi-fluid, almost liquid substance, containing nitrogen; it is white, contains a considerable amount of water, and has a slight odour resembling that of caprylic acid; it is only slightly soluble in water, and insoluble in alcohol and ether. Sulphuric and nitric acid dissolve and decompose it; potash evolves ammonia from it. When moist it absorbs oxygen and evolves carbonic acid, and, when left to itself, dries up to thin, shining, transparent films, devoid of structure, and resembling the mucin of the garden snail.

When recently produced, it is highly phosphorescent, and the production of light is owing to oxidation. It is secreted in phosphorescent animals by a special organ, and appears to be consumed [? by oxidation] in producing light nearly as fast as it is formed. Its light is nearly monochromatic, and its spectrum principally de-

veloped between the lines E and F. In an impure state noctilucin can be obtained from the surface of various fish when highly phosphorescent, also from the glow-worm, by pressing the luminous matter collected by the scalpel through porous filtering-paper. It is secreted in a pure form by the luminous centipede (*Scolopendra electrica*).

**NOHLITE.** This mineral, from Nohl near Kongelf, Sweden, very nearly resembles the samarskite from the Ural, but is distinguished from it by a rather considerable percentage of water. It is compact, of a black-brown colour, and is opaque and brittle. The fracture is uneven and splintery, and the lustre highly vitreous. Hardness 4.5-5.0; specific gravity 5.04. Before the blowpipe it slowly melts at the edges to a dull glass, and feebly decrepitates through loss of water.

Analysis gave the following numbers:—

Nb <sup>2</sup> O <sup>5</sup>	ZrO <sup>2</sup>	UO	YO	CeO	CaO	MgO, MnO	FeO	CuO	H <sup>2</sup> O
50.43	2.96	14.43	1.36	0.25	4.67	0.28	8.09	0.11	4.62 = 100.20

agreeing approximately with the formula  $2(\text{RO.Nb}^2\text{O}^5) + 3\text{H}^2\text{O}$ . (A. E. Norden-skiöld, *Jahrbuch f. Mineralogie*, 1872, 552).

**NONANE, C<sup>9</sup>H<sup>20</sup>.** See PARAFFINS.

**NONYLIC ACID, C<sup>11</sup>H<sup>22</sup>O<sup>2</sup>.** See PELARGONIC ACID.

**NUCLEIN.** A substance resembling mucin existing in pus-corpuscles and in the nuclear structures of the yolk of the hen's egg. See F. Miescher, 'Ueber die Chemische Untersuchung der Eiterzellen' (*Med.-chem. Unters.* 1871, 411). 'Die Kerngebilde im Dotter des Hühnerereies' (*ibid.* 509). Hoppe-Seyler, 'Ueber die Chemische Zusammensetzung des Eiters' (*ibid.* 486); also *Chem. Soc. J.* [2], ix, 742-747. *Gmelin's Handbook*, English Edition, xviii, 467.

**NUTMEG OIL** (Wright, *Chem. Soc. J.* [2], xi, 549). The purest commercial oil of nutmeg is resolvable by fractional distillation into the following bodies: 1. A soft brown resin (about 2 p.c. of the oil) not volatile at 300°, and having the composition C<sup>10</sup>H<sup>16</sup>O<sup>4</sup>. 2. Liquids boiling at 260°-280° and 280°-290°, whose composition may be represented by the formula (C<sup>10</sup>H<sup>16</sup>O<sup>2</sup>)<sub>n</sub>. 3. An oxidised oil, C<sup>10</sup>H<sup>16</sup>O, boiling at 212°-218°. 4. A mixture boiling at 173°-179° (about 15 p.c. of the original oil), of a terpene, C<sup>10</sup>H<sup>18</sup>, with a small quantity of cymene. 5. A hydrocarbon boiling at 163°-164°, consisting of a terpene with a trace of cymene, amounting to 70 p.c. of the original oil.

From these results it may be inferred that the hydrocarbon boiling at 167°, called by Gladstone myristicene (*Chem. Soc. J.* [2], x, 3), is a mixture of two or more terpenes with perhaps a little cymene.

The oxidised body, C<sup>10</sup>H<sup>16</sup>O, is myristicol (p. 833). It is converted by heat into an isomeric (or polymeric) modification boiling at a higher temperature, and subsequently into a resin having the same composition. Myristicol treated with dehydrating agents yields cymene, and when treated with phosphorus pentachloride it is converted into a compound C<sup>10</sup>H<sup>14</sup>Cl, which is resolved by prolonged boiling into hydrogen chloride and cymene.

The cymene contained in the portion of the nutmeg hydrocarbon which boils at 163°-164°, may be isolated by treating the mixture with sulphuric acid so as to polymerise the terpene present (the cymene is not altered by the treatment), then shaking with water and distilling in a current of steam. The cymene thus obtained is quite pure, and amounts to about 8 p.c. of the hydrocarbon boiling at 163°-164°.

The terpene of nutmeg-oil may be converted into cymene by combining it with bromine and distilling the resulting dibromide C<sup>10</sup>H<sup>16</sup>Br<sub>2</sub>, whereby it is resolved into 2HBr and C<sup>10</sup>H<sup>14</sup>.

**NUTRITION.** For the most important contributions to the chemistry of Animal Nutrition since the publication of the *First Supplement* of this Dictionary, see the articles GASTRIC JUICE, GLYCOGEN, MUSCULAR TISSUE, RESPIRATION, and URINE, in the present volume.

## O

**OATS** (Fr. *Avoine*, Ger. *Hafer*). Cultivated oats include *Avena sativa*, the common oat; *A. orientalis*, Tartar oats, also largely cultivated; and *A. brevis*, and other species grown for hay in some parts of the continent. The varieties, especially of the first-named species, are very numerous, and differ much from each other as to the colour of the husk, the weight per bushel of the grain, the length and character of the straw, &c. Oats having a high weight per bushel (44-46 lbs.), owe this quality in great measure to the thinness of their husk and skin; they yield the best proportion of meal, 60 p.c. and upwards. Oats with a low weight per bushel (some varieties 35-38 lbs.) have a thicker husk and skin, yield a smaller proportion of meal, and are used as food for horses. From this difference in the character of the husk, oats present a wide range in chemical composition. The following table shows the average composition and extent of variation of oat-grain and straw of good quality. The composition of oat-husk is taken from old analyses by Norton; the figures for oat-chaff are Wolff's average.

	Number of analyses	Water	Albuminoids	Fat	Carbo-hydrates	Fibre	Ash
Oats . . .	24	12.07 10.5-14.8	12.87 8.6-18.5	6.05 4.2-7.1	53.85	10.76 6.3-13.4	3.50 2.7-5.1
Oat-husk . .	—	11.09	1.67	1.07	80.21		5.96
Oat-chaff . .	—	14.30	4.00	1.50	28.2	34.00	18.00
Oat-straw . .	16	14.68 11.3-19.5	3.69 1.1-7.0	1.60 1.1-2.7	34.47	40.46 31.8-48.9	5.10 3.6-6.3

When the husk is removed from the oat, in making oatmeal, the proportion of fibre and of ash is greatly reduced, while the amount of albuminoids and carbo-hydrates rises. Thomson gives 15.61 p.c. as the average of albuminoids in oatmeal; Voelcker, 15.68; some chemists place it as high as 17; very few perfect analyses have been published. The fat in oatmeal is about 7 p.c., the ash 1.5. From its high contents in albuminoids and fat, oatmeal is probably the most concentrated food supplied by cereal grains. It is interesting to observe that, while the removal of the bran from wheat reduces the nitrogenous and fatty contents of the flour, the removal of the husk from oats has precisely the opposite effect, so that the finer the oatmeal the richer it is in these ingredients.

The embryo of the oat, as probably of all other seeds, is especially rich in nitrogen; Lenz (*Jahresh. Agri. Chem.* 1870-2, 4) found it to contain nitrogen equal to 26.7 p.c. of albuminoids.

The nature of the albuminoids in oats has been thoroughly studied by Krouser (*J. pr. Chem.* cvii. 17). The principal albuminoid is oat-legumin, the avenine of Johnston; it is obtained by acting on oatmeal with very weak solution of potash in the cold, precipitating the solution with acetic acid, and purifying the precipitate by resolution and precipitation, treatment with ether, and finally by boiling with 60 p.c. alcohol to remove gliadin. Thus purified it contains, ash deducted, C. 51.63, H. 7.40, N. 17.16, O. 22.93, S. .70. It agrees in most respects with the legumin of peas, but in its high percentage of sulphur, and some of its properties, more resembles the glutenin of Ritthausen. Oatmeal also yields by extraction with alcohol a small quantity of oat-gliadin, similar in properties and composition to the gliadin of wheat, but containing more hydrogen and sulphur; it is indeed the richest in sulphur of the vegetable albuminoids. The percentage composition of purified oat-gliadin, ash deducted, is C. 52.59, H. 7.65, N. 17.71, O. 20.39, S. 1.66.

For the composition of the fat of oats and oat-straw, see the article **FAT** in this volume.

Oat-straw has, on an average, a higher nutritive value than the straw of wheat or barley; it contains less woody fibre and a larger amount of soluble carbo-hydrates and albuminoids. The albuminoids vary greatly, being high when the straw is green, and diminishing rapidly in quantity as the straw ripens; for the sake of the improved quality of the straw oats are frequently harvested before ripening is completed. The straw at the time of harvest contains 30-40 p.c. of water even when fully ripe, and much more if cut earlier; the analyses quoted above refer to straw which has become dry in the stack.

Way found in six specimens of oats an average of 2.34 p.c. of sulphur, and in four specimens of straw an average of 1.68 p.c., both on the dry substance.

The average composition of the ash of oats, oat-straw, &c., is as follows:—

	Number of analyses	Per cent. ash in dry	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>2</sup>	SiO <sup>2</sup>	Cl	Co <sup>2</sup>
Oats, whole	22	3.3	15.7 { 9.8-24.3	2.5 { 8.2-3	3.7 { 8.4-13	7.2 { 0.7-4.9	.7 { 2.1-1	21.7 { 32.3-9.7	1.5 { 4.0-1	45.7 { 56.5-32.3	1.6-0	none
Oats, husked	3	2.1	26.4	—	5.0	9.0	.6	43.8	17.4-0	2.7	.3	—
<i>Avena nuda</i>	1	—	33.4	—	3.6	11.8	.8	46.9	—	2.4	—	—
Oat-husk	4	6.7	4.7	4.2	8.2	1.1	1.3	1.5	6.0	75.9	.7	—
Oat-chaff	3	8.3	7.7 { 13.1-3.6	4.8 { 5.7-4.0	7.6 { 12-1.9	2.8 { 5.4-4	1.7 { 2-4	4.0 { 6.3-1	5.0 { 9.6-2.5	64.6 { 72.8-59.9	1.4	—
Oat-straw with chaff	3	5.2	21.2	4.2	7.0	3.8	1.5	5.1	3.4	49.6	3.9	4.1-0
Whole plant when ripe:												
Bretschneider	1	5.4	19.1	5.3	5.4	5.0	.4	10.1	3.9	49.2	2.0	—
Arendt	1	5.2	34.5	.7	11.6	5.0	.5	11.2	4.2	28.6	4.6	—

The variations in the ash of oats are seen to be very considerable; they are mainly due to the varying proportion of husk. Oats with thin husk give an ash with high potash and low silica, but when the husk is thick the silica is high and the potash low. This is made evident by comparing the ash analysis of the husk with that of oats deprived of husk. The ash analyses of husked oats are by Norton and Johnston, and the ash analyses of the husk by Norton and Fromberg; the methods used for these analyses were very imperfect, but the general character of the ash is made evident. The ash analysis of *Avena nuda*, in which the husk is naturally separated from the grain, is by F. Schulz. The ash analyses of oat-chaff are by Way and Marchand, with one quoted by Anderson; they vary greatly. Norton found in seven specimens of oat-chaff a mean of 16.94 p.c. of ash in the dry, containing 60-80 p.c. of silica; he detected manganese in several specimens of grain and husk. The analyses of oat-straw with chaff are by Way and Ogston. The results of Bretschneider and Arendt are very different as regards potash, lime, silica, and chlorine; the explanation lies in the fact that Bretschneider operated on an average sample of an oat-crop, Arendt on selected vigorous and perfect plants. Arendt showed the great difference which the luxuriance of the plant makes in the composition of the ash by examining separately very vigorous, strong, and weak plants at different stages of growth; the analysis of the whole plants at the time of blossom gave:—

	Alkalies	Lime	Magnesia	Ferrio Oxide	Phosphoric acid	Sulphuric acid	Silica	Chlorine
Very luxuriant oat-plant . . .	45.3	6.1	2.9	.4	8.2	4.8	27.0	6.7
Strong oat-plant . . .	34.3	5.4	2.3	.5	8.5	4.1	39.9	5.8
Weak oat-plant . . .	30.4	5.2	2.3	1.0	8.8	5.0	42.0	4.7

Luxuriant plants always contain a greater amount of soluble ash constituents than they actually require.

Arendt found that in the stem and leaves of the oat all the sulphates and chlorides, and nearly all the phosphates, existed in a soluble condition, but that nearly all the silica, save in the lower part of the stem, was in an insoluble state. By determining sulphates in the green plant, he ascertained that the distribution of sulphates and of sulphur was very different. Thus, immediately after blossom, the lower part of the stem contained no sulphates, while they were abundant in the upper leaves; both parts, however, contained sulphur in considerable quantity.

The composition of the different parts of the oat plant at different stages of its growth has been thoroughly studied by Norton (*Amer. Jour. Sci.* [2], iii. 223, 318), by Bretschneider (*J. pr. Chem.* lxxvi. 193), by Arendt (*Wachsthum der Haferpflanzen*, and *Jahresb. Agri. Chem.* 1858-9, 124), and by Fittbogen (*Jahresb. Agri. Chem.* 1864, 128). From this abundance of material we select Bretschneider's figures dealing with the oat crop as a whole, and Arendt's results for the various parts of the plant.

Bretschneider analysed the stem, leaves, and seed of an oat-crop in five stages of growth—I. June 19, 58 days after sowing; the fourth and fifth leaf generally developed. II. June 29; the ear had left its sheath. III. July 8; full bloom. IV. July 28; commencement of ripening. V. August 6; fully ripe. The results for the second period were imperfect.



*Composition of an Oat Crop in various Stages of Growth.*

Contents in 100 parts of the dry crop					Contents in kilos. per hectare			
	I.	III.	IV.	V.	I.	III.	IV.	V.
Organic matter . . .	91.43	94.04	94.67	94.60	1087	3817	4758	6032
Ash . . . . .	8.57	5.96	5.33	5.40	102	242	268	344
Carbon . . . . .	46.22	48.76	47.91	46.89	550	1979	2408	2900
Hydrogen . . . . .	6.23	6.53	6.33	5.88	74	265	318	376
Oxygen . . . . .	35.39	36.96	37.65	39.40	421	1460	1892	2512
Nitrogen . . . . .	3.69	2.79	2.78	2.43	43	113	140	156
Water in fresh . . .	70.80	73.47	63.77	35.17	4698	11241	8846	3459

*Composition of the Ash.*

In 100 parts					In kilos. per hectare			
	I.	III.	IV.	V.	I.	III.	IV.	V.
Potash . . . . .	28.96	25.60	25.90	19.14	29.52	61.93	69.38	65.91
Soda . . . . .	6.40	8.67	4.16	5.29	6.54	20.97	11.17	18.19
Lime . . . . .	5.66	6.46	5.19	5.43	5.77	15.62	13.90	18.69
Magnesia . . . . .	5.34	5.25	4.98	5.02	5.44	12.70	13.34	17.29
Ferric oxide . . . .	1.22	.39	.31	.39	1.24	1.04	.83	1.34
Phosphoric acid . . .	7.95	9.17	9.61	10.13	8.10	22.18	25.74	34.88
Sulphuric acid . . .	5.57	2.46	1.99	3.89	5.67	5.95	5.33	13.39
Silica . . . . .	36.28	40.00	45.57	49.17	36.97	96.77	122.07	169.28
Chlorine . . . . .	3.38	2.68	2.94	2.00	3.45	6.25	7.90	6.68

From these figures it appears that the crop attains its maximum weight at the time of blossoming, after which the amount of water rapidly diminishes, while the organic matter and ash continue to increase. Assimilation is most rapid shortly before blooming. The organic matter of the crop increases far more quickly than the ash, the percentage of which at first rapidly, and then more slowly, diminishes. The individual organic elements are assimilated in different proportions at the various stages of growth, which will be most clearly seen by the following statement, showing the proportion of each taken up for 100 of carbon assimilated.

Period	I.	Carbon	Nitrogen	Hydrogen	Oxygen
"	III.	100	7.81	13.4	73.6
"	IV.	100	4.92	13.3	72.5
"	V.	100	6.15	12.3	100.3
"		100	2.61	10.6	106.5

It is evident that the formation of albuminoids takes place chiefly in the earlier part of the plant's life, while carbo-hydrates are the principal formation in the later stages. The low proportion of hydrogen assimilated at the close seems to point to the formation of lignose.

Among the ash constituents of the oat-crop it appears that but little potash or lime is assimilated after the time of blossom, while of magnesia, and especially of phosphoric acid and of silica, more considerable quantities are taken up during the later stages of growth.

Arendt, as already mentioned, selected vigorous and perfect oat-plants, and determined the composition of various parts of the plant in five stages of growth; his results are given in the table, p. 866. At Period I. the plants were 0.31 meter high; three leaves were unfolded. At Period II. the height was 0.63 m.; the ear was half protruded. At Period III. the height was 0.84 m.; blossoming had just finished. At Period IV. the height was unchanged; ripening had commenced. At Period V. perfect ripeness was attained. Arendt's crop was sown later and reaped earlier than that of Bretschneider, and the plants taken for analysis were clearly far more luxuriant than those

operated on by the last-named investigator. Only a few points in the table can be referred to.

The amount of woody fibre apparently reaches its maximum at the time of blossoming, after which other carbo-hydrates are developed. Fibre reaches its highest percentage in the dry matter of the stem, especially in the lower part. Fat is most abundant in the leaf, the lower leaves after blossoming containing 9-10 p.c. of fat and wax. Albuminoids in the young plant are most abundant in the leaf, in the ripe plant in the ear; a transference of nitrogen from the leaf to the ear is evident after blossoming. The leaf is the part richest in ash; after blooming the upper leaves contain much more ash than the lower ones. Norton even found that the upper half of an oat-leaf contained more ash than the lower half. The ash of the stem is exceedingly rich in potash, that of the leaf contains less potash, but a much larger quantity of lime (compare Ulbricht's results with clover, FODDER PLANTS). The ash of the stem, contrary to popular notion, is poorest in silica of any part of the plant; the maximum of silica is in the leaf. Phosphoric acid and magnesia find their maximum in the ash of the ear; a transference of phosphoric acid from the leaf and stem to the ear is plainly seen. This relation of the ash constituents of the stem, leaf, and ear is abundantly confirmed by Bretschneider. In Arendt's 'ash' carbonic acid is deducted; the ash of the ripe stem must have contained a large quantity.

Fittbogen is the only experimenter on the oat-plant who has included the roots in his investigation; his plants were grown in glass pots and examined at three periods. From the time when three leaves were unfolded, the roots diminished in weight, and especially in ash constituents; the transference of matter from the root took place chiefly just before the time of blossoming. Hellriegel examined the plants grown by Fittbogen, and found that each oat-plant (growing at the rate of 32 in a cubic foot of soil) possessed an average of 150 feet of root fibre.

The influence of different classes of manures on the growth of oats, and their effect on the composition of the crop, are best illustrated by the results of Messrs. Lawes and Gilbert. The following figures, kindly communicated by the authors, show the average produce of black Tartarian oats grown for five successive years on the same land.

*Produce of Tartar Oats with various Manures.*

Manures per acre	Dressed corn	Straw and chaff	Total produce	Corn to 100 straw	Weight per bushel of dressed corn
	bushels	owts.	lbs.		lbs.
No manure . . . . .	19½	10½	1988	72	33½
Mixed cinereal manure . . . . .	24½	13½	2532	70	35
Ammonium salts, 400 lbs. . . . .	47	28½	5188	65	36½
Nitrate of sodium, 550 lbs. . . . .	47½	27½	5110	69	35½
Ammonium salts, 400 lbs. with } cinereals	50	41½	7100	58	37
Nitrate of sodium, 550 lbs. with } cinereals	57½	35	6347	67	35½

The mixed cinereal manure consists of superphosphate, with potassium, sodium, and magnesium salts. The ammonium salts are mixed chloride and sulphate; they supply the same quantity of nitrogen as the 550 lbs. of nitrate of sodium.

The results plainly show that the oat-plant, like other graminaceous crops, is unable to supply itself from the natural resources of the soil and atmosphere with an amount of nitrogen sufficient to produce a full crop, even when abundantly supplied with ash constituents. The best result in the experiments is obtained where nitrogenous and cinereal manures are applied together.

The effect of the above manures on the composition of the crop is seen in the following table, which shows that the dry matter in the corn is practically not altered by manuring, while in the straw the dry matter is a little lower in the more luxuriant crops. The amount of dry matter is, however, considerably affected by season, the variation being greatest in the straw. The percentage of ash in the corn exhibits considerable variation by manuring, but the variation is not so much connected with the supply of ash constituents to the plant as with the weight per bushel of the grain; where the grain is best developed, and contains the largest proportion of kernel to husk, there the ash is at a minimum, and the weight per bushel at a maximum; where the specific

Percentage Composition of Oat-corn variously manured.

	Dry matter			Ash in dry			Nitrogen in dry		
	Highest	Lowest	Mean	Highest	Lowest	Mean	Highest	Lowest	Mean
No manure . . .	86.1	81.6	84.1	4.75	3.86	4.29	—	—	—
Cinereal manure . .	86.4	81.7	84.1	4.51	3.69	4.07	2.13	1.47	1.85
Ammonium salts . .	86.7	82.2	84.7	3.69	3.22	3.50	—	—	—
Nitrate of sodium . .	86.5	80.9	84.2	4.01	3.42	3.60	—	—	—
Ammonium salts and cinereals. }	87.0	82.7	84.7	3.51	3.00	3.32	2.34	1.83	2.05
Nitrate of sodium and cinereals. }	86.4	82.8	84.6	3.81	3.30	3.52	2.35	1.83	2.10

Percentage Composition of Oat-straw variously manured.

No manure . . .	82.4	77.8	80.3	11.54	8.03	10.40	—	—	—
Cinereal manure . .	83.1	78.1	80.6	12.05	7.68	10.54	.516	.326	.461
Ammonium salts . .	82.3	77.8	79.6	9.88	7.69	8.73	—	—	—
Nitrate of sodium . .	82.8	76.6	79.5	8.21	6.57	7.30	—	—	—
Ammonium salts and cinereals. }	82.6	75.3	78.4	10.75	7.38	8.64	.574	.344	.481
Nitrate of sodium and cinereals. }	82.7	75.0	79.1	8.44	6.68	7.57	.674	.356	.504

gravity is lowest, and the proportion of husk greatest, the ash reaches its maximum. In the straw the percentage of ash varies even more than in the corn. The supply or non-supply of ash constituents has here clearly some effect on the result, especially in seasons of defective ripening, as seen in the column of highest percentages; but in favourable seasons the percentage is mainly affected by the bulk of the crop, the heavier crops containing least ash. The straw manured with nitrate of sodium contains distinctly less ash than that manured with sulphate and chloride of ammonium. The percentage of nitrogen both in grain and straw is but little affected by its supply, the effect of season is far more considerable; nitrogen is lowest in both grain and straw in seasons of favourable ripening, and high when ripening is incomplete.

An average out-crop of 45 bushels of grain, at 42 lbs. per bushel, and 2835 lbs. of straw (3 of straw to 2 of grain), will remove from the land in lbs. per acre about the following quantities:—

	Nitrogen	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	Cl	SiO <sup>2</sup>	Total ash
Grain . . .	37.8	8.5	1.4	2.0	3.0	.4	11.8	.8	—	24.8	54.3
Straw . . .	14.2	29.6	5.0	9.8	5.3	2.1	7.1	4.8	5.5	69.3	139.7
Total . . .	52.0	38.1	7.3	11.8	9.2	2.5	18.0	5.6	5.5	94.1	194.0

R. W.

**OBOLUS.** Analyses of *Obolus* shells from the lower Silurian sandstone of Eathland have been made by A. Kupffer (*Jahresb. f. Chem.* 1870, 1337); they consist, mainly of a fluorapatite, having the composition  $\text{CaF}_2 \cdot 3\text{CaP}^2\text{O}_8$ .

**OCTANE, C<sub>8</sub>H<sub>18</sub>.** *Octyl Hydride*, Normal Octane, or dibutyl, prepared by the action of sodium on normal butyl iodide, obtained by Lieben a. Rossi's process from butyric acid, boils at 123°–125°, and has a specific gravity of 0.7032 at 17°. It appears, therefore, to be identical with the octane obtained from methyl-hexyl carbinol and from sebic acid, also with that which Zincke obtained from primary octyl alcohol (1st Suppl. 877).

**OCTAMINE (or TETRAMINE) CHROMIUM-COMPOUNDS.** See CHROMIUM (p. 386).

**OCTAPO-TETRAMORPHINE.** See MORPHINE (p. 823).

**OCTENE, or OCTYLENE-COMPOUNDS.**—The chlorhydrin,  $C^8H^{14}(OH)Cl$ , is formed by treating octene with aqueous hypochlorous acid not containing more than 0.75 p.c.  $HClO$ . The product freed from unaltered octylene by heating it to  $125^\circ$ , and passing a rapid stream of carbonic anhydride through it, is a mobile slightly yellowish liquid, having a camphorous odour and burning taste, insoluble in water, but soluble in ether and in alcohol, decomposed by boiling. Sp. gr. = 1.003 at  $0^\circ$ , and 0.987 at  $31^\circ$ . Heated to  $180^\circ$  in a digestion-tube with sticks of potash and a little water, it yields a liquid which boils at  $145^\circ$ , has a specific gravity of 0.831 at  $15^\circ$ , and yields by analysis 72.9 p.c. carbon and 11.7 hydrogen. Now octene oxide,  $C^8H^{14}O$ , requires 75.0 C. and 12.5 H., whereas heptene oxide,  $C^7H^{12}O$ , requires 73.7 C. and 12.3 H. Probably, therefore, the product consisted mainly of heptene oxide, resulting from the oxidising action of the hypochlorous acid on the octene chlorhydrin. When octene was treated with a 2 to 3 p.c. solution of hypochlorous acid, no octene chlorhydrin was obtained, the hypochlorous acid in the more concentrated state exerting an oxidising as well as a substituting action. The product yielded, by fractional distillation, a liquid boiling at  $206^\circ$ – $208^\circ$ , and having the composition of heptene-chlorhydrin,  $C^7H^{12}(OH)Cl$ . The portion boiling above  $208^\circ$  contained a still larger proportion of chlorine (P. de Clermont, *Bull. Soc. Chim.* [2], xiii. 404).

Octene glycol,  $C^8H^{14}(HO)^2$ , boiled for ten hours with nitric acid containing rather more than  $4H^2O$  to each  $N^2O^3$ , yields a solution of oxalic acid on which there floats an oil containing, besides unattacked octene glycol, an acid which remains liquid at  $-10^\circ$ . A barium salt prepared from it contained 22.95 p.c. metal, and could not therefore be either a suberate or a caprylate. In another oxidation not carried quite so far, a solid crystalline acid was formed, the barium salt of which contained from 38.8 to 38.7 p.c. metal (P. de Clermont, *loc. cit.*)

**OCTETHYL-SILICIC ETHER.** See SILICIC ETHERS.

**OCTYL ALCOHOLS,  $C^8H^{18}O$ .** Primary iso-octyl alcohol or isohexptyl carbinol, obtained by Zincke from the volatile oil of the seeds of *Heracleum sphondylium* (1st *Suppl.* 878), may also be obtained from the oil of *Heracleum giganteum*, which contains the corresponding acetic ether (Franchimont a. Zincke, *Deut. Chem. Ges. Ber.* iv. 420).

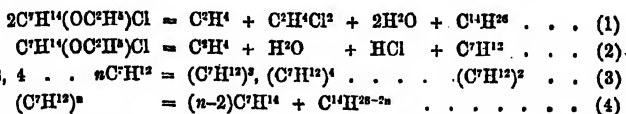
*Secondary Octyl Alcohol or Methyl-hexyl Carbinol,*  $\begin{matrix} CH^3 \\ | \\ C^6H^{13} \end{matrix} CHOH$ , is produced, together with methyl-hexyl ketone, by distilling sodium ricinoleate with excess of alkaline hydrate; and Neison has lately shown, by a very careful investigation, that these are the sole products of the reaction (*Chem. Soc. J.* [2], xii. 837–851). The alcohol, when purified from the ketone as completely as possible, boils, according to Schorlemmer's latest determination, at  $177^\circ$ – $178^\circ$  (*Chem. Soc. J.* [2], xii. 1029). Former determinations gave  $181^\circ$ , but Schorlemmer regards the recent determination as the more trustworthy, first because the pure alcohol had been prepared from a larger quantity of material, and secondly, because it appears to be a general law that a normal secondary alcohol containing the group  $-CHOH-CH^3$ , boils at the same temperature as the normal primary alcohol which contains 1 atom of carbon less. This may be seen from the following table, including only such alcohols as have been most minutely studied:—

	Bolling-point		Bolling-point
$C^6H^{12}.OH$ . . .	$97^\circ$ – $98^\circ$	$C^8H^{18}.OH.CH^3$ . . .	$86^\circ$ – $98^\circ$
$C^6H^{11}.OH$ . . .	$137^\circ$	$C^8H^{16}(OH).CH^3$ . . .	$136^\circ$
$C^6H^{10}.OH$ . . .	$116.5^\circ$ – $177.5^\circ$	$C^8H^{14}(OH).CH^3$ . . .	$177^\circ$ – $178^\circ$

**CENANTHOL, or CENANTHYLIC ALDEHYDE,  $C^8H^{14}O$ .** Preparation.—Schiff (*Zeitschr. f. Chem.* vi. 74) prepares this aldehyde by distilling half a litre of castor-oil in a 2½-litre vessel over a gas flame till the mass just begins to froth up. The distillation-vessel is then emptied, again charged with ½-litre of the previously warmed oil, and this operation is repeated till 10 kilograms of material have been treated. The products consist of 1.27 kilograms of purified cenanthol, 50 grams of less pure cenanthol, to be purified by combination with sodium bisulphite, &c., 100 grams of acrolein, and a quantity of oily bye-products. The viscid, spongy residue of the distillation may be completely liquefied by gentle heating, and ultimately distilled almost without residue. An addition of the oily bye-products above mentioned diminishes the frothing.

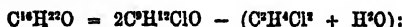
*Reaction with Hydrochloric acid.*—Williamson, by passing hydrochloric acid gas through an alcoholic solution of cenanthol, and treating the product with water, ob-

tained an oily liquid which he regarded as cenanthylic ether,  $C^8H^{14}O^2$  (iv. 178). Schiff, on the other hand (*Zeitschr. f. Chem.* vi. 74), finds that the chief product of this reaction is heptene-chlorethylin, or heptene-methyl chloride,  $C^7H^{14}\begin{smallmatrix} Cl \\ | \\ OC^2H^3 \end{smallmatrix}$ . This compound is a light oil insoluble in water, easily soluble in alcohol and ether, gradually decomposed by contact with warm water. It could not be obtained pure, as it is completely decomposed by distillation. The decomposition, which is very complicated, may, according to Schiff, be approximately represented by the following equations:—

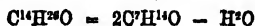


If the first distillation be interrupted at  $320^\circ$ , there remains a brown viscid residue consisting of hydrocarbons,  $C^{14}H^{2n-2}$ , and others, which residue, when heated, is resolved, as indicated by equation (4), into bodies of relatively lower boiling point. Hence, by continually separating from the resulting distillates the portions which go over below  $320^\circ$ , and again distilling the residues, the relative quantity of the lower-boiling hydrocarbons will continually increase at the expense of those of higher-boiling point. From a product thus obtained, the following compounds were isolated by repeated fractionation: (1.) Heptene,  $C^7H^{14}$ , from fractions  $90^\circ$ – $100^\circ$ ; (2.) a yellow oil,  $C^{14}H^{28}$ , from fractions  $245^\circ$ – $260^\circ$ ; (3.) a very viscid oil,  $C^{14}H^{28}$ , having the consistence of turpentine in the cold, from fractions  $320^\circ$ – $330^\circ$ ; (4.) a pitch,  $C^{14}H^{18}$ , as residue of the distillation when carried on to  $350^\circ$ . The formulae assigned to these bodies are supported by closely agreeing analyses. The four bodies just mentioned constitute, however, only the smallest portion of the entire product of the decomposition, the principal portion consisting of mixtures which could not be separated into definite products.

The product of the first distillation of the heptene-chlorethylin contains an aldehydic body boiling at  $240^\circ$ , the separation of which succeeds only when the product is distilled by itself. It slightly reduces ammoniacal silver nitrate on boiling, and unites with sodium bisulphite to a scarcely crystalline mass. Its analysis gave numbers which agreed with the formula:



considering, however, the imperfect purity of the substance, the result might also be represented by the formula:



which requires the same amount of carbon and 1 p.c. less hydrogen (Schiff).

Cenanthol, treated in the cold with solid potassium hydrate, is converted into two polymeric modifications, one a crystalline solid, the other an oily liquid. Both yield, on distillation, cenanthol and condensation-products formed from it by abstraction of water (Borodin, *Deut. Chem. Ges. Ber.* v. 480).

**CENANTHYLIC ACID**,  $C^8H^{14}O^2 = C^8H^{12}.CO^2H$ . This acid, first obtained by Tilley in 1841 by oxidising castor-oil with nitric acid, is also produced by oxidation of cenanthol with nitric acid or with chromic acid; by the oxidising action of nitric acid on oleic acid and on Chinese wax; by that of chromic acid on heptylic alcohol from heptane; and by the action of potash on cenanthol (iv. 177). The boiling-points of the acid obtained by these several processes have been variously stated at  $212^\circ$ – $222^\circ$ . Tilley's acid, which boiled at  $148^\circ$ , was doubtless impure. Franchimont (*Ann. Ch. Pharm.* clxv. 23), by converting hexyl alcohol from hircalium oil into the nitril,  $C^8H^{14}N$ , and decomposing this compound with caustic potash, obtained a heptylic or cenanthylic acid, which boiled at  $223^\circ$ – $224^\circ$ , the whole column of mercury being in the vapour.

To obtain more precise data as to the identity or diversity of the acids from these several sources, a further examination of cenanthylic acid produced by oxidation of cenanthol has been made by Grimshaw & Schorlemmer (*Chem. Soc. J.* [2], xi. 1073).

To prepare the acid, 300 grams of cenanthol from castor-oil, boiling at  $150^\circ$ – $160^\circ$ —not quite pure, but still containing some acrolein and other products—was gradually added to a warm solution of 300 grams of potassium dichromate, 400 sulphuric acid, and 900 water. After the action was over the flask was connected with a reversed condenser, and the liquid boiled for some hours. After cooling, the two layers of

liquid were separated, the lower one, containing some cenanthylic acid in solution, was distilled, and the distillate saturated with soda. The upper layer was well shaken with caustic soda, to remove chromic oxide, and the solution of the sodium salt evaporated. On adding sulphuric acid to the concentrated liquid, cenanthylic acid separated out as an oily layer, which was washed with water and dried over phosphorus pentoxide.

The acid thus obtained contains some acrylic acid, and begins therefore to boil a little above  $140^{\circ}$ ; the boiling point soon rises to  $200^{\circ}$ , and then more slowly to  $230^{\circ}$ ; at the same time the liquid blackens, and a dark residue is left in the flask. On rectifying the higher-boiling portion, it again leaves a dark residue, and water is formed; the distillates must therefore be dried over phosphorus pentoxide, and the fractional distillation continued, until the acid has a constant boiling point, does not act any longer on phosphorus pentoxide, and volatilises without leaving a residue.

**Properties.**—Pure cenanthylic acid is a limpid, oily liquid, boiling under a pressure of 763 mm. at  $223^{\circ}$ – $224^{\circ}$ . The cold acid has a faint smell, like that of tallow, but on heating it becomes unpleasantly sour and pungent. In a freezing mixture it soon solidifies to plates, or large broad needles. It melts and solidifies at  $-10.5^{\circ}$ . Franchimont's heptylic acid melted at  $-8^{\circ}$ , but he adds that, from repeated experiments, the melting point seemed to be two degrees lower. Schorlemmer's heptylic acid from heptane did not solidify in a freezing mixture; but as the heptane from which it was prepared had to be separated by fractional distillation from an isomeric boiling at  $7^{\circ}$  lower, and from an octane boiling about  $17^{\circ}$  higher, it probably still retained some of these hydrocarbons, and would yield an heptylic acid contaminated with the corresponding acids.

The specific gravity of cenanthylic acid, compared with water at  $4^{\circ}$ , is 0.9350 at  $0^{\circ}$ , 0.9288 at  $0^{\circ}$ , and 0.9235 at  $28^{\circ}$ ; that of heptylic acid at  $24^{\circ}$  is 0.9212.

**Ethyl Cenanthylate**,  $C^7H^{12}(C^2H^5O_2)^2$ , prepared by mixing equal volumes of the acid and absolute alcohol with half a volume of strong sulphuric acid, and purified by washing with water and dilute soda-solution, drying over calcium chloride and finally over phosphorus pentoxide, and fractional distillation, boils at  $187^{\circ}$ – $188^{\circ}$ , with the whole mercurial column immersed in the vapour. It has a specific gravity of 0.8735, and does not solidify at  $-20^{\circ}$ . Ethyl heptylate boils at about the same temperature, has a specific gravity of 0.874, and does not solidify at  $-18^{\circ}$ .

**Metallic Cenanthylates.** The *potassium salt* was obtained only as a transparent jelly. The *sodium salt* crystallises by slow cooling in slender rhmifid needles; from a strong solution quickly cooled it separates in a gelatinous mass in which distinct needles may be recognised by the microscope. Sodium heptylate from Franchimont's acid possesses similar properties.

**Barium Cenanthylate**,  $Ba(C^7H^{12}O_2)^2$ , crystallises in thin plates or flat needles, 1.700 grams of which dissolve in 100 c.c. of water. The barium salt of the acid from heptane has very similar properties: 100 c.c. of water dissolve 1.744 grams of it. The barium salt of Franchimont's acid also crystallises in anhydrous thin plates; its solubility was not determined.

**Calcium Cenanthylate**,  $Ca(C^7H^{12}O_2)^2 + H_2O$ , forms very thin, flat, fascicular needles which dry up to a silky mass. 100 c.c. of its solution saturated at  $8.5^{\circ}$  contain 0.17 gram  $CaO$ . The calcium salts of the acid from heptane and from Franchimont's acid exhibit similar properties and composition; 100 c.c. of the solution of the former contain also 0.17 gram  $CaO$ .

**Zinc Cenanthylate**,  $Zn(C^7H^{12}O_2)^2$ , obtained by adding zinc sulphate to the sodium salt, and crystallising the dried precipitate from absolute alcohol, separates in small needles or short four-sided prisms, accordingly as the solution is cooled quickly or slowly.

The crystals, which contain neither alcohol nor water, melt at  $130^{\circ}$  and decompose at higher temperatures. Franchimont's zinc heptylate crystallises also in short prisms melting at  $131^{\circ}$ – $132^{\circ}$ ; they contain, however, 2 molecules of alcohol.

**Lead Cenanthylate**,  $Pb(C^7H^{12}O_2)^2$ , is a heavy precipitate not very freely soluble in boiling water, but it may be crystallised therefrom, and is thus obtained in thin, small, iridescent, rhombic prisms, or in stellate groups of flat needles. The precipitated salt softens at  $79^{\circ}$ – $80^{\circ}$ , and melts to a transparent liquid at  $90^{\circ}$ . The crystallised salt begins to soften at  $88^{\circ}$ , liquefies completely at  $94^{\circ}$ – $96^{\circ}$ , and resolidifies at  $75^{\circ}$ – $76^{\circ}$ . Lead heptylate is a similar salt, melting, according to Franchimont, at  $78^{\circ}$ – $80^{\circ}$ .

**Copper Cenanthylate**,  $Cu(C^7H^{12}O_2)^2$ , falls down as a soft mass, on adding copper sulphate to a solution of the sodium salt, but on standing the precipitate becomes granular. It is quite insoluble in boiling water, but dissolves readily in absolute

alcohol, and is obtained by spontaneous evaporation in green silky needles, or short prisms.

The copper salt of the acid from heptane, and Franchimont's copper heptylate, are similar precipitates. The former could not, however, be obtained in crystals, but separated from the alcoholic solution as a liquid, drying up to an amorphous mass. Franchimont's copper heptylate also is first obtained in drops, which afterwards solidify to groups of short prisms.

*Silver Ceanthylate*,  $\text{AgC}^{14}\text{H}^{12}\text{O}_2$ , is a white precipitate, crystallising from boiling water, in which it is but sparingly soluble, in small, woolly needles.

From the facts above detailed it appears most probable that the heptylic acid prepared from heptane is identical with ceanthylic acid from castor-oil, the barium and calcium salts of the two acids having the same properties, composition, and solubility. Heptylic acid prepared by Franchimont's method also bears the greatest resemblance to ceanthylic acid, only the copper and zinc salts exhibiting slight differences. Whether these are essential or not, can be decided only by preparing the salts under exactly the same conditions, and comparing them directly with each other.

There can be no doubt that ceanthylic acid and heptylic acid are both normal compounds; this, however, does not imply that they are really identical. It is not only possible, but even very probable, that the hexyl alcohol from hemeleum oil, as well as the heptylic acid obtained from it, are optically active, while ceanthylic acid probably does not possess this property.

**OILS.** On the Spectra of Fixed Oils, see J. Müller (*Dingl. pol. J.* cxviii. 529; *Jahresb. f. Chem.* 1870, 175).

On the Testing of Fixed Oils: Flückiger (*Arch. Pharm.* [2], cxliv. 120; *Jahresb.* 1870, 1049); H. Ludwig (*Arch. Pharm.* [3], i. 1-33).

On the Valuation of Oil-seeds: H. Vohl (*Dingl. pol. J.* cc. 110, 236; *Jahresb.* 1871, 1097; *Chem. Soc. J.* [2], ix. 761, 960).

On the Quantity and Composition of Fixed Oils in Various Seeds, see FAT (p. 506 of this volume).

On the Specific Gravities and Expansion-Coefficients of Fixed Oils: Stillwell (*American Chemist* [2], i. 407; *Jahresb.* 1871, 109).

On the Reactions of Fixed Oils with Sulphuric Acid: G. P. Clarke (*Chem. News*, xxiii. 145).

On the Properties of Drying Oils: Sacc (*Compt. rend.* lxxiii. 1274; *Chem. Soc. J.* [2], x. 183).

On the Boiling of Drying Oils for the preparation of Varnish: C. W. Vincent (*Chem. News*, xxiii. 107, 207).

**OILS VOLATILE or ESSENTIAL.** The essential oils of plants consist for the most part of mixtures of hydrocarbons with oxidised constituents, the latter being sometimes products of the direct oxidation of the hydrocarbon, in which case they are usually viscid resins, while in other cases the relation between the two constituents of the oil is not apparent.

*Hydrocarbons* (Gladstone, *Chem. Soc. J.* [2], x. i).—The specific gravities, boiling points, and optical properties of several of these hydrocarbons, were determined by Gladstone in 1864, and are given in the table on p. 188, vol. iv. of this Dictionary. Gladstone now proposes to distinguish them by the following names:

Hydrocarbon from Bay	Laurylene.
" " Calamus . . . . .	Calamene.
" " Dill . . . . .	Anetheno.
" " Elder . . . . .	Sambuceno.
" " Eucalyptus amygdalina . . . . .	Eucalypteno.
" " Myrtle . . . . .	Myrteno.
" " Nutmeg . . . . .	Myristiceno.
" " Rosewood . . . . .	Rhodieno.

*Polymeric Groups.*—The hydrocarbons from essential oils may be arranged in three polymeric groups having the formulæ  $\text{C}^{14}\text{H}^{14}$ ,  $\text{C}^{16}\text{H}^{16}$ ,  $\text{C}^{18}\text{H}^{18}$ ; the first comprising the great mass of these hydrocarbons—turpentine, orange, caraway, nutmeg, anise, thyme, myrtle, and twenty others; the second, those derived from cloves, rosewood, cubeba, calamus, cascarrilla, and patchouli; while the third group is represented only by colophene. It is probable, however, that parncaputene belongs to this last group, also that some of the substances named colophene, obtained from various sources, are not identical, but only isomeric, with colophene from turpentine.

These groups are distinguished from one another by several properties, especially by the vapour-density of the hydrocarbons belonging to them, that of the first being nearly equal to, though generally a little above, the theoretical density for  $C^{10}H^{18}$ , viz. 4.71. Among the bodies of the second group, which should have theoretical density 7.06, cedrene was found by Walter to have a vapour-density of 7.6, and the hydrocarbons from calamus and patchouli have, according to Gladstone's determinations, the vapour-densities 6.80 and 7.2 respectively. The experimental vapour-density given in Gmelin's Handbook for colophene exceeds that which would be required by the formula  $C^{20}H^{32}$ .

The following table gives a general view of the properties and reactions of the hydrocarbons of the three groups—

	10-Carbon group	16-Carbon group	20-Carbon group
Formula . . . . .	$C^{10}H^{18}$	$C^{16}H^{24}$	$C^{20}H^{32}$
Vapour-density . . . . .	4.7	7.1	—
Character of liquid . . . . .	limpid	viscid	more viscid
Specific gravity at 0° . . . . .	0.846–0.880	0.904–0.927	0.939
Refractive index for A, at 20° . . . . .	1.457–1.467	1.488–1.497	1.5084
Dispersion . . . . .	about 0.027	about 0.020	0.031
Sensitiveness . . . . .	about 48	about 43	41
Boiling point . . . . .	160°–176°	249°–280°	315
Action of sulphuric acid . . . . .	polymerises	doubtful	none
Solubility in aqueous alcohol . . . . .	freely soluble	sparingly soluble	insoluble
Combination with HCl . . . . .	$C^{10}H^{18}.2HCl$ and $C^{10}H^{18}.HCl$	$C^{16}H^{24}.HCl$ and in smaller proportions	very small quantity

There is no difference in specific refractive energy between the several groups. The various members of the 10- and 16-carbon groups have powerful odours and rotate the plane of polarisation strongly, sometimes in one direction, sometimes in the other.

## OILS CONTAINING OXYGEN.

Oil	Specific gravity at 20°	Boiling point	Refractive Index A, at 20°	Dispersion	Sensitiveness	Specific refractive energy	Circular polarisation*
Citronellol, Penang . . . . .	0.8742	200	1.4563	0.0251	50	0.6219	—
Do. Ceylon . . . . .	0.875	200	1.4594	0.0262	46	0.6251	— 13
Absinthol . . . . .	0.9267	217	1.4543	0.0243	43	0.4903	+ 184
Cajeputol, from the leaves of <i>Melaleuca leucodendron</i> . . . . .	60	174	1.4532	0.0213	45	—	— 2?
<i>Melaleuca ericifolia</i> . . . . .	0.8060	173	1.4560	0.0239	48	—	+ 30
<i>Melaleuca linariifolia</i> . . . . .	0.8985	173	1.4651	0.0263	46	—	+ 11
<i>Eucalyptus oleosa</i> . . . . .	0.9075	171–176	1.4563	0.0227	44	—	+ 10
Carvol . . . . .	0.9530	227	1.4886	0.0345	46	51.26	+ 145°
Dill carvol . . . . .	0.9562	—	1.4801	0.0333	45	51.15	+ 108°
* Menthol I. . . . .	0.9515	225	1.4839	0.0326	44	50.86	— 103°
Menthol II. . . . .	0.9304	225	1.4791	0.0311	42	51.00	— 114°
Myristicool . . . . .	0.9468	224	1.4848	0.0312	46	51.21	+ 81°
Oil of Rose . . . . .	0.881	216	1.4647	0.0283	47	—	—
„ Indian geranium . . . . .	0.884	—	1.4602	0.0295	59	—	— 8
„ <i>Atherosperma moschatum</i> . . . . .	1.0386	224	1.5143	0.0460	46	—	+ 10
„ <i>Lign aloes</i> . . . . .	640	200	1.4601	0.0280	—	—	—

\* Menthol I. was prepared by fractional distillation; menthol II. from the compound with hydrogen sulphide.



**Testing of Volatile Oils.**—On the mode of distinguishing volatile oils one from the other by mixing them with strong sulphuric acid, or with sulphuric acid and carbon sulphide, whereby mixtures are produced varying in colour and transparency, see Hager (*Zeitschr. anal. Chem.* 1870, 534); Flückiger (*Arch. Pharm.* [2], cxliv, 144; also *Jahresb. f. Chem.* 1870, 1048). Hager finds that many of the more expensive oils are adulterated with sassafras-oil, which addition may easily be detected by the cherry-red colour produced on diluting the sulphuric acid mixture with alcohol.

To detect oil of turpentine in other essential oils, Zeller some years ago proposed the use of alcohol, the slight solubility of turpentine-oil in that liquid giving rise to a turbidity in the mixture. This test has hitherto been regarded by many who have tried it as applicable only when the turpentine is present in considerable quantity; but, according to Dragendorff (*N. Rep. Pharm.* xxii. 1), this want of delicacy arises from the use of alcohol in an undiluted state; for when the oil to be examined is miscible in all proportions with absolute alcohol, it forms with this liquid a mixture capable of dissolving a very considerable proportion of oil of turpentine. If, however, the alcohol be diluted until 2-4 volumes of it are required to dissolve 1 volume of the oil, it will be found that the presence of a small quantity of turpentine is indicated by the decreased solubility of the adulterated oil in the diluted alcohol.

To determine the solubility of an oil in alcohol, 2 c.c. of it are placed in a stoppered bottle, and the alcohol is gradually added from a burette, the mixture being well shaken after each addition. The termination of the experiment is known by the liquid becoming clear. A suspected sample being now similarly treated, it will be found that, if turpentine be present, a larger proportion of alcohol will be required.

In testing essential oils for turpentine by means of alcohol, it must be borne in mind that some other oils, such as those of juniper, savin, eucalyptus, and copaiba are but slightly soluble in dilute alcohol, and that they may, when mixed with other oils, give rise to appearances similar to those produced by oil of turpentine. Moreover, in some cases changes take place in oils which have been kept for a long time, and these must be considered in applying the alcohol test for turpentine.

For the details concerning each individual oil we must refer to the original paper, which also contains a table showing the solubility of turpentine-oil from various sources in spirit of various degrees of concentration.

For the detection of alcohol in essential oils, Hager (*Chem. Centr.* 1871, 821) adds to the oil a piece of solid tannin, which becomes moist and slimy if any spirit is present.

For the estimation of the alcohol, Böttger (*ibid.* 1872, 742) agitates the oil in a graduated tube with an equal volume of pure glycerin. On leaving the liquid to separate, the increase in the volume of the glycerin indicates the amount of alcohol present.

Essential oils, prepared by distillation with water, often retain some of that liquid even when they appear quite clear. The water may be detected by mixing the oil, with several times its volume of petroleum ether (the so-called benzine), whereby a turbidity is produced, owing to the separation of globules of water (G. Leuchs, *J. pr. Chem.* [2], vi. 159).

**OLEFINES.** On the Production of Olefines from Paraffin by Distillation under Pressure, see PARAFFIN.

**OLIBANUM.** By distilling this gum-resin with water in a cast-iron retort, an oil is obtained constituting about 7 p.c. of the resin taken; alcohol extracts from the residue about 72 p.c. of resin, and the remainder is gum. The crude oily distillate boils between 160° and 170°, and contains oxygen, as Stenhouse previously observed (*iv.* 198). By fractional distillation a hydrocarbon, olibene, boiling at 156°-158°, of turpentine-like odour, and sp. gr. 0.863 at 12°, is obtained, together with a small quantity of an oxidised substance boiling above 175°, and not yielding a hydrocarbon when treated with sodium. Olibene is soluble in alcohol and in ether, and is resinised by nitric acid; it absorbs 1 mol. of hydrogen chloride, giving, on standing, a crystalline camphor-like body, C<sup>10</sup>H<sup>16</sup>.HCl, which melts at 127°.

The resin, exhausted as above by alcohol, melts readily, and yields by dry distillation traces of an organic acid and an oil which boils above 360°, and contains less oxygen than the resin itself (Kurbatow, *Zeitschr. f. Chem.* [2], vii. 201).

**OLIGOCLASE.** See FALSIFAR (pp. 510-514).

**OLIVE-OIL.** This oil in its natural state contains in solution a yellowish substance which, when the oil is treated with acids or with caustic soda, gives rise to the well-known greenish coloration. By exposure to sunshine this colouring matter is essentially altered, the oil being thereby decolorised and no longer exhibiting a green-

ish colour when treated with the reagents above mentioned. Moreover, other changes take place at the same time in the constituents of the oil, the olein in particular being greatly altered, and acquiring the fundamental property of *elaidin*, namely, that of not solidifying in contact with nitrate of mercury mixed with nitrous products. At the same time free acids are formed, and the oil acquires a rancid taste and odour.

From these results it appears that the method suggested by some authors of distinguishing olive-oil from other oils by means of sulphuric acid, caustic soda, and nitrate of mercury, can be depended upon only when the oil is in its natural state, not altered by exposure to sunshine (L. Moschini, *Gazzetta chimica italiana*, i. 580).

On the detection of *Earthenut-oil* in Olive-oil, see p. 443.

**OLIVIN.** The olivin of the Pallas meteoric iron has been examined by N. v. Kokscharow (*Jahrb. f. Mineralogie*, 1870, 778), who, in addition to the forms discovered by G. Rose, has observed the following:— $\frac{1}{2}P$ ,  $\frac{1}{4}P$ ,  $mPn$ ,  $\frac{1}{2}P\infty$ ,  $\frac{1}{4}P\infty$ , and  $P\infty$ , which, excepting the last two, are new for olivin. Numerous measurements gave, for the ratio of principal axis, macrodiagonal and brachydiagonal, 1.25928 : 2.14706 : 1. An examination of thin sections showed that the channels observed by G. Rose are empty, and run parallel to the principal axis. An analysis by N. v. Leuchtenberg gave:—

SiO <sup>2</sup>	SnO <sup>2</sup>	MgO	FeO	MnO	Al <sup>2</sup> O <sup>3</sup>	Sp. gr.
40.24	0.08	47.41	11.80	0.29	0.06 = 99.88	3.3398

The following analyses by Philipp of the olivin in the olivin-rock of the Dreiser Wogher Basalt, in the Eifel, is given by Rammelsberg (*Zeitschr. geol. Gesellschafts.* xx. 899):—

SiO <sup>2</sup>	MgO	FeO	Sp. gr.
41.25	48.85	9.90 = 100.0	3.36

The analysis gives Fe : Mg = 1.0.

The olivin-rock above mentioned has been analysed by Rammelsberg with the following results: A. Decomposable portion; B. undecomposable; C. The decomposable portion calculated to 100 parts.

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup> , Cr <sup>2</sup> O <sup>3</sup>	MgO	CaO	FeO	Chrom-iron	
A. .	27.41	—	34.24	trace	6.85	—	= 68.50
B. .	15.57	1.74	8.35	2.29	1.74	1.00	= 30.69
C. .	40.02	—	49.98	trace	10.00	—	= 100

The numbers in C, compared with those in the analysis of olivin above given, show that the latter only is decomposed by acids, while the augitic substance, as shown by the mere trace of CaO, is scarcely attacked.

Kraubat, in Upper Styria, is mentioned by R. v. Drascho (*Min. Mitth.* 1871, 57) as a new locality of olivin rock.

F. Sandberger (*Jahrb. f. Mineralogie*, 1871, 622) mentions a patito as a hitherto overlooked constituent of olivin rock. In the rock of Lherz, A. Hilger found 0.096 to 0.112 p.c. P<sup>2</sup>O<sup>5</sup>. Traces of cobalt were also found in it.

**OPAL.** An elaborate investigation of numerous opals has been made by H. Behrens (*Wien. Acad. Ber.* 2te. Abth. lxiv. 519; *Jahrb. f. Mineralogie*, 1872, 316). The following minerals occur as admixtures with the opal mass: hydrophane (recognisable by impregnation with colouring matters), quartz, ferric oxide and hydrate, nontronite, green earth, serpentine, arsenic sulphide, and lime. Organic matter occurs but rarely and in small quantity.

Opals may be distinguished, according to their microscopic structure, as homogeneous and mixed opals. To the former belong fire-opal, glass-opal, noble opal, and hyalite; the latter sometimes exhibits an irregular, mostly stratified, occasionally also an oolitic structure, due in some cases to concretions of tridymite. The play of colours is attributed by Behrens to their reflecting lamellae, which appear to have been originally imbedded horizontally in the still soft opal mass, but afterwards to have become fissured and notched during the irregular desiccation of the mass. That an unequal contraction has taken place is shown by the strong double refraction. All noble opals are biaxial. The horizontally arranged cavities to which Brewster ascribed the play of colours, Behrens was unable to detect.

An opal from Waddela plain, Abyssinia, has been analysed by Maskelyne & Flight (*Chem. Soc. J.* [2], ix. 2). It is of a dark smoky green colour, with occasional layers of white opal, like the prase-opal of Faros, weathered on the exterior, and passing into yellowish-white cacolong:

$\text{SiO}_2$	$\text{H}_2\text{O}$	$\text{Fe}^{+3}$	$\text{Mn}^{+2}$	$\text{CaO}$	$\text{MgO}$	
sol.	insol.					
90.562	2.049	5.666	0.933	trace	0.137	0.311 = 99.648

Most, if not all, of the water, is given off at  $100^\circ$ .

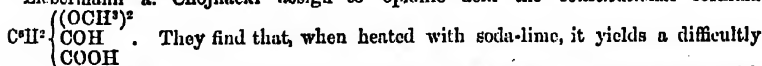
Opal from S. Piero in Elba is described by G. vom Rath (*Zeitschr. geol. Gesellsch.* xxii. 643). It occurs in flat lumps collected in veins in a disintegrated serpentine bordering on granite. The fresh nearly colourless opal has a sp. gr. of 1.990 (at  $21^\circ$ ), and loses 9.48 p.c. by ignition. After ignition its sp. gr. is 1.815. No microscopic tridymite was found in it. Black opal containing garnet, like that of Meronitz in Bohemia, also occurs in loose blocks at S. Piero. Sp. gr. before ignition, 2.062 (at  $21^\circ$ ); after ignition, 1.953. Loss by ignition, 6.36.

**OPIANIC ACID**,  $\text{C}^{10}\text{H}^{10}\text{O}^6$ . By the action of sulphuric acid upon opianic acid, Anderson, in 1855, obtained a colouring matter which yielded with alumina and iron mordants, colours like those of madder, and was regarded by him as probably identical with alizarin (*Chem. Soc. Qu. J.* viii. 277). This colouring matter has been further investigated by Liebermann a. Chojnacki (*Deut. Chem. Ges. Ber.* iv. 194). To prepare it, opianic acid is heated to  $180^\circ$  with 30 times its weight of strong sulphuric acid, whereupon the liquid becomes violet-red. On pouring the cooled mass into water, the impure colouring matter separates in black flocks, which may be obtained of yellowish-brown colour by repeated solution in caustic soda, filtration, and precipitation with acid. By dissolving them in ether and evaporating, yellowish-red crusts are obtained, which may be purified by several repetitions of the entire process.

This colouring matter distilled with zinc-dust yields a colourless sublimate which has not been analysed, but appears from its properties to be anthracene. The colouring matter dissolves in potash with the colour of purpurin, but is distinguished from this compound, as well as from alizarin, by the violet-red colour of its solution in strong sulphuric acid, which, on the other hand, exactly resembles that of rufgallic acid. This acid, however, dissolves in potash with blue colour, and is quickly precipitated from the solution in contact with air, a reaction not exhibited by the colouring matter from opianic acid. With lead and barium solutions coloured precipitates are obtained; mordants are dyed with colours resembling those produced by rufgallic acid more than those of alizarin. On subliming the colouring matter, the greater part of it is carbonised. The analysis of the unsublimed substance gave numbers agreeing nearly with the formula  $\text{C}^{10}\text{H}^{10}\text{O}^6$ , but Liebermann a. Chojnacki are of opinion that this formula does not express the true composition of the substance.

Hypogallic acid treated with sulphuric acid does not yield any colouring matter, but is decomposed, with evolution of gas.

Liebermann a. Chojnacki assign to opianic acid the constitutional formula



volatile oil having exactly the odour of methyl-pyrocatechin. Heated to  $200^\circ$  with dilute hydrochloric acid, it yields, with elimination of carbon dioxide, several well-crystallised acids of more simple constitution.

**OPIUM.** On the estimation of Morphine in Opium, see MORPHINE (p. 818).

In opium grown at Hancock, Vermont (U.S.) W. Procter (*Arch. Pharm.* [2] cxlii. 237) found 16.75 p.c. morphine, 2.00 narcotine, 5.25 meconic acid, 11.00 caoutchouc, fatty substances and resins, 22.00 insoluble matter, 38.50 substances soluble in water and different from the salts of morphine and narcotine, and 5.00 water.

In opium from the south coast of the Victoria Colony, J. S. Ward (*Pharm. J. Trans.* [3], i. 628), found 9 p.c. morphine, 4 narcotine, and 6 meconic acid.

**OPIUM BASES.** O. Hesse (*Ann. Ch. Pharm. Suppl.* band viii. 261; *Zeitschr. f. Chem.* [2], vii. 641; *Deut. Chem. Ges. Ber.* iv. 693). The papers here cited contain a continuation of Hesse's observations on the rarer opium bases (1st *Suppl.* p. 883).

In these later experiments Hesse has examined the mother-liquors obtained in the Robertson-Gregory process (iv. 1051) for extracting morphine (conversion into hydrochlorides by addition of calcium chloride to the opium extract, and crystallisation of the morphine, pseudomorphine, and codeine salts from the liquor). On addition of an excess of ammonia to the mother-liquor diluted with its own bulk of hot water, an inconsiderable resinous precipitate of lantopins is produced, the other bases remaining in solution. By agitation of the filtrate with ether, and of the ethereal extract with acetic acid, a mixture of acetates is obtained. Caustic soda added in excess precipitates papaverine, narcotine, thebaine, some cryptopine, and the three

new bases, protopine, laudanose, and hydrocotarnine, while the alkaline filtrate contains in solution lanthopine, laudanine, some cryptopine, meconidine (?) and codamine. These last are again converted into acetates by the ether process, and the liquid is neutralised with ammonia. A little lanthopine separates after twenty-four hours, and the filtrate yields, with ammonia, a precipitate soluble in boiling dilute alcohol. On cooling, crystals of a mixture of laudanine and cryptopine separate. The alcoholic filtrate was found to contain no meconidine, although this base should be here obtained, whence Hesse concludes that the meconidine is decomposed by the Robertson-Gregory process, though not by the process adopted in his former experiments. By evaporation of the alcoholic solution, and treatment with ether, a solution was formed, from which codamine was obtained, either by addition of fused calcium chloride, which causes water, colouring matters, and crystals of codamine to separate, or by conversion into acetate, thence into hydriodide, and purification of the latter.

The precipitate insoluble in caustic soda is digested with diluted alcohol, and acetic acid added till litmus-paper is faintly reddened by it. Addition of three times the volume of boiling water produces a crystalline precipitate of papaverine and narcotine (these bases not neutralising acetic acid). The filtrate freed from alcohol by evaporation, gives, on addition of strong hydrochloric acid, a precipitate of cryptopine hydrochloride; but this method is not to be recommended, as the acid converts some of the thebaine into thebaineine (a non-crystalline isomeride), which interferes with the separation of the other bases. A better plan is to add tartaric acid, which causes a copious crystallisation of thebaine bitartrate. The mother-liquor of this is neutralised by ammonia, and mixed with 3 p.c. of its weight of sodium bicarbonate made into a paste with water. After about a week, a black pitchy mass separates. The filtrate from this gives with ammonia a precipitate which is treated with boiling benzene, the filtrate being also extracted with benzene. Cryptopine and protopine then remain undissolved, while on shaking the benzene solution with a saturated aqueous solution of sodium bicarbonate, laudanose crystallises out; and the benzene filtrate from this, treated with gaseous hydrogen chloride, yields hydrochloride of hydrocotarnine.

Hesse describes narcotine as existing in the mother-liquors of the Robertson-Gregory process, but does not state how, or at what stage, it is separated from the other bases.

*Pseudomorphine*,  $C^{17}H^{10}O^4$ , is found only occasionally in opium, being observed only once in good Smyrna opium during four years. It gives crystals with  $H^2O$  and  $4H^2O$ . It forms a nitro-substitution product, which rapidly disappears in nitric acid. Reducing agents (sulphurous acid, sulphuretted hydrogen, nascent hydrogen) have no action on it.

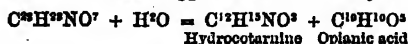
*Lanthopine*, like pseudomorphine, narcotine, and papaverine, does not neutralise acetic acid. It gives no colour with ferric chloride.

*Laudanine*,  $C^{20}H^{23}NO^4$ , and *Cryptopine* are separated by dilute caustic soda, which dissolves the latter only sparingly. The filtrate is treated with sal-ammoniac, the precipitate thereby formed is dissolved in acetic acid, and potassium iodide added, whereby a hydriodide of laudanine, free from cryptopine, is obtained. Concentrated caustic potash solution gives a crystalline compound with laudanine. Hesse formerly found  $C^{20}H^{23}NO^3$  as the formula of laudanine, but he now adopts  $C^{20}H^{23}NO^4$ . For cryptopine he gives the formula  $C^{21}H^{23}NO^3$ . The body analysed by T. and H. Smith, to which they attributed the formula  $C^{21}H^{23}NO^3$ , was contaminated with thebaine. The observation of these chemists, that the base forms two hydrochlorides, the one containing  $C^{21}H^{23}NO^3 \cdot HCl \cdot 5H^2O$ , the other,  $C^{21}H^{23}NO^3 \cdot 2HCl \cdot 6H^2O$ , is erroneous, only one,  $C^{21}H^{23}NO^3 \cdot HCl \cdot 6H^2O$ , being produced. Nitric acid of sp. gr. 1.06 forms nitro-cryptopine, which forms well characterised salts, the base being anhydrous, crystalline, and melting at  $185^\circ$ . Its formula is  $C^{21}H^{22}(NO^2)NO^3$ , which is the same as that of crystallised nitropapaverine, with which, however, it is not identical, the latter containing water of crystallisation =  $C^{21}H^{22}(NO^2)NO^4 \cdot H^2O$ .

*Codamine*,  $C^{20}H^{23}NO^4$ , melts at  $126^\circ$  when crystallised from benzene, and at  $120^\circ$  when from alcohol or ether; ferric chloride gives a fine dark-green colour, with separation of ferric oxide; it appears to form compounds with caustic alkalis. Hesse now adopts the formula  $C^{20}H^{23}NO^4$ , instead of the earlier one,  $C^{20}H^{23}NO^3$ .

*Narcotine*,  $C^{28}H^{33}NO^7$ .—Hesse corroborates the formula ascribed to this base by Matthiessen and Foster, in place of the older one,  $C^{28}H^{33}NO^7$ ; the base is separated from papaverine by solution in boiling water containing one-third part of oxalic acid; on cooling, the acid papaverine oxalate crystallises out; this process is repeated several times, and, finally, the narcotine is precipitated by ammonia and crystallised from boiling alcohol. It melts at  $176^\circ$ , and decomposes at a few degrees higher. On

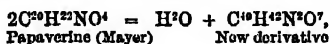
boiling with baryta-water, narcotine forms a base much resembling hydrocotarnine readily soluble in ether, which Hesse supposes to be formed by the reaction—



and he infers that narcotine is decomposed by water in the same way, and not in the manner stated by Matthiessen & Wright (*1st Suppl.* 863), viz:—



**Papaverine**,  $\text{C}^{21}\text{H}^{21}\text{NO}^4$ .—Hesse formerly showed that the pure base has this composition, and not that which was formerly attributed to it, viz.,  $\text{C}^{22}\text{H}^{22}\text{NO}^4$ , and he considers that the supposed new derivative obtained from it by E. L. Mayer (*Deut. Chem. Ges. Ber.* iv. 128), by the action of zinc chloride, and considered by him to be formed by the reaction—



is nothing but papaverine, Mayer's numbers agreeing well with those required for the formula  $\text{C}^{21}\text{H}^{21}\text{NO}^4\cdot\text{HCl}$ .

Papaverine treated with nitric acid of sp. gr. 1.06 is converted into nitropapaverine,  $\text{C}^{21}\text{H}^{20}(\text{NO}^2)\text{NO}^4 + \text{H}^2\text{O}$ , which, when crystallised in the dark, is colourless, but becomes yellow in the light; the water of crystallisation is given off only at  $163^\circ$ , when the substance melts and becomes coloured.

**Protopine**,  $\text{C}^{20}\text{H}^{19}\text{NO}^4$ , is separated from cryptopine by precipitation of the solution of the mixed hydrochlorides with strong hydrochloric acid; the protopine salt is horny, and adheres to the sides of the vessel, and is easily freed from the cryptopine salt by a little washing with water: a quantity of material that gave 80 grams of cryptopine, gave only about  $1\frac{1}{2}$  of protopine. It gives no colour with ferric chloride.

**Laudanosine**,  $\text{C}^{21}\text{H}^{21}\text{NO}^4$ , crystallises from alcohol, hot benzene, or ether; it melts at  $89^\circ$ , and gives no colour with ferric chloride.

**Hydrocotarnine**,  $\text{C}^{12}\text{H}^{12}\text{NO}^3 + \frac{1}{2}\text{H}^2\text{O}$ , dissolves readily, and without coloration, in alcohol, acetone, chloroform, benzene, and ether, and crystallises readily from the latter. The crystals melt at  $50^\circ$ , losing all their water of crystallisation at  $57^\circ$ . At  $100^\circ$ , a great loss of weight is perceptible, without any appreciable alteration in composition; it cannot, however, be distilled under the ordinary pressure.

Pure sulphuric acid gives, on warming, distinctive colorations with the opium alkaloids, the tints being much altered in many cases by traces of impurity of iron or oxides of nitrogen. By this means Hesse divides the opium alkaloids into groups:—

I. a. Morphine, Pseudomorphine, Codeine.	Dirty dark-green (morphine group).
β. Laudanine, Codamine, Laudanosine.	Dirty red-violet (laudanine group).
II. Thebaine, Cryptopine, Protopine.	Dirty green to brown-green (thebaine group).
III. α. Papaverine.	Dark violet (papaverine group).
β. Narceine, Lanthopine.	Black-brown to dark-brown (narceine group).
IV. Narcotine, Hydrocotarnine.	Dirty red-violet (different shade from that of I. β) (narcotine group).

Group I. β give a dark-violet tint with acid containing iron, while IV. give still a dirty-red violet, as with the pure acid.

**OPIUM WAX.** See CERYLIC ETHERS (p. 276).

**ORANGE-PEEL OIL.** (Wright & Piosse, *Chem. Soc. J.* [2], ix. 1186; Wright, *ibid.* xi. 552). It has been shown by Soubeiran & Capitaine, also by Gladstone, that the essential oil of orange-peel consists mainly of a hydrocarbon  $\text{C}^{18}\text{H}^{14}$ , called hesperidene, boiling at  $174^\circ$ . This result is confirmed by the experiments of the authors above cited. The pure oil begins to boil at  $175^\circ$ , and 97.8 p.c. goes over below  $180^\circ$ , the remainder consisting of a soft yellow resin, inodorous when quite free from hesperidene, having a bitter aromatic taste, and only slightly soluble in alcohol either cold or hot. It contains 75.6 p.c. carbon, and 9.7 hydrogen, agreeing with the formula  $\text{C}^{18}\text{H}^{14}$ . On distilling it, a few drops passed over between  $180^\circ$  and  $280^\circ$ ; the portion collected at  $240^\circ$ – $260^\circ$  had the composition  $\text{C}^{16}\text{H}^{12}\text{O}^2$ . The small portion distilling over between  $210^\circ$  and  $230^\circ$  appeared to be identical with myristic oil,  $\text{C}^{18}\text{H}^{16}\text{O}$ .

\* With reference to this, Wright observes that the experiments by himself and Matthiessen above quoted have distinctly shown that pure meconin may be obtained by heating narcotine with water in sealed tubes (*Chem. Soc. J.* [3], ix. 738).

Hesperidene does not contain cymene, for on agitating it with strong sulphuric acid (to polymerise the terpene), diluting with water after 24 hours, and distilling in a current of steam, a distillate is obtained which does not yield a trace of terephthalic acid when treated with chromic acid mixture. Nevertheless the heat developed by agitating hesperidene with sulphuric acid is sensibly less than that which is evolved by the action of sulphuric acid on an equal quantity of the nutmeg hydrocarbon boiling at  $163^{\circ}$ – $164^{\circ}$ , although this latter contains a considerable quantity of cymene which is not acted on by the sulphuric acid (p. 862). A similar difference is observed when bromine is dropped into the two hydrocarbons, the nutmeg product developing much more heat than that from orange-oil, although the product in each case is a dibromide,  $C^{10}H^{16}Br^2$ . This difference in the quantities of heat evolved from the two isomeric hydrocarbons under similar circumstances is doubtless related to the diversities in their boiling-points and other physical properties.

Hesperidene dibromide is resolved by heat into hydrogen bromide and cymene:  $C^{10}H^{16}Br^2 = 2HBr + C^{10}H^{14}$  (p. 419). When hesperidene is boiled for several days with a large excess of dilute chromic acid mixture, about 1 p.c. of it is oxidised to myristical  $C^{10}H^{16}O$ ; the greater portion is, however, completely oxidised to carbonic acid and water; and, on distilling the product, a distillate is obtained containing acetic acid, with perhaps a trace of formic acid. No terephthalic acid is produced (Wright).

**ORCIN**,  $C^7H^8O^2$ . This compound may be formed synthetically from toluene. On heating chlorotoluene,  $C^7H^5Cl.CH^3$ , to  $100^{\circ}$  for some hours with sulphuric acid, two isomeric chlorocresylsulphurous acids,  $C^7H^4Cl.SO^2H$ , are produced, which may be separated by the fractional crystallisation of their barium salts. The less soluble salt, *barium  $\alpha$ -chlorocresylsulphite*,  $(C^7H^4ClSO^2)^2Ba + 2H^2O$ , forms beautiful colourless rhombic plates, whilst the other, viz.: *barium  $\beta$ -chlorocresylsulphite*  $(C^7H^4ClSO^2)^2Ba + 1\frac{1}{2}H^2O$ , which is much more soluble, crystallises in mammillated tufts consisting of small crystalline grains. The *potassium  $\alpha$ -chlorocresylsulphite*, obtained by double decomposition from the corresponding barium salt, forms nacreous plates, moderately soluble both in cold water and in boiling alcohol. When this salt is fused with twice its weight of potassium hydrate, it becomes brown, and gives off hydrogen, while orcin, salicylic acid, and cresol are produced. The aqueous solution of the fused mass is agitated, first with benzene to remove the salicylic acid and cresol, then with ether, which dissolves the orcin and leaves it in an impure state on evaporation. This orcin when purified is identical both in its properties and crystalline form with the orcin prepared from the lichens, which is therefore a toluenediphenol,  $C^7H^4.HO.HO$ .

Orcin is the principal product of this reaction, the cresol and salicylic acid formed at the same time resulting from the action of the potassium hydrate on the potassium cresylsulphite; the latter is produced from the potassium chlorocresylsulphite by the reducing action of the hydrogen formed during the fusion (Vogt u. Henninger, *Compt. rend.* lxxiv. 1107).

**Chlor- and Brom-orcins.** These compounds, some of which are described in vol. iv. pp. 213, 214, have lately been further examined by Stenhouse (*Proc. Roy. Soc.* xx. 72), who has also obtained the penta-compounds.

**Pentachlororcine**,  $C^7H^3Cl^5O^2$ , is formed when a solution of orcin is added to a pulpy mixture of chlorine hydrate and water, or to a mixture of potassium chlorate and hydrochloric acid, care being taken to keep the chlorinating mixture in excess. The crude product is then purified by crystallisation from carbon sulphide. It forms large colourless prisms, which melt at  $120.5^{\circ}$ . It is moderately soluble in carbon sulphide and benzene, readily in ether. It is but very slightly soluble in water, to which, however, it communicates an exceedingly disagreeable and persistent bitter metallic flavour. It appears to suffer decomposition when boiled either with alcohol or with water, trichlororcine being one of the products formed in the latter case.

**Pentachlororcine hypochlorite**,  $C^7H^3Cl^5O^3 = C^7H^3Cl^5O^2.HClO$ .—When orcin is treated with hydrochloric acid and a solution of calcium hypochlorite, the two latter being in excess, a turbid solution is obtained, which, after the lapse of 24 hours, deposits white crystals. These, when crystallised from benzene, form colourless transparent prisms of great dispersive power, which melt at  $140.5^{\circ}$ . This compound is very soluble in ether, but, unlike pentachlororcine, only sparingly soluble in carbon sulphide. It is decomposed by hydriodic acid and phosphorus, but the product has not yet been examined.

**Trichlororcine**,  $C^7H^3Cl^3O^2$ , is readily obtained by the reduction of pure pentachlororcine with hydriodic acid and amorphous phosphorus. It is moderately soluble in boiling water, and crystallises out on cooling in colourless transparent needles, which melt at  $123^{\circ}$ . It is but sparingly soluble in carbon sulphide, moderately in

petroleum oil and benzene, and excessively soluble in ether and alcohol. It dissolves in hot glacial acetic acid, from which it crystallises in thin transparent plates which become white and opaque on the addition of water. Heated to 180° with hydriodic acid and phosphorus, it is reconverted into orcin (Stenhouse).

**Pentabromorcin**,  $C^6H^3Br^5O^2$ , is easily prepared by adding an aqueous solution of orcin, with constant agitation, to a mixture of bromine and water, taking care that the bromine is in slight excess. Its solution in carbon sulphide, in which it is moderately soluble, yields very large and almost colourless transparent crystals, melting at 126°. It is almost insoluble in water, very soluble in alcohol and ether, and moderately so in benzene. Pentabromorcin, when boiled with phosphorus and strong hydriodic acid, passes into solution, probably as orcin; but with very weak hydriodic acid, tribromorcin is formed, identical with that described by Stenhouse, and subsequently examined by Laurent and Gerhardt, and by Lamparter (iv. 213).

Pentabromorcin, heated to 150°-160°, gives off 2 at. bromine, leaving the compound  $C^6H^3Br^3O^2$ , which crystallises from chloroform in minute yellow scales. This com-

pound may be regarded as tribromorcinquinone,  $C^6H^3Br^3 \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$  (Liebmann & Dittler,

*Ann. Ch. Pharm.* cxlix. 252).

**Iodorcin**,  $C^6H^3IO^2$ , is prepared by dissolving 1 part of orcin and 2 of iodine in 6 parts of ether, and gradually adding 9 parts of finely-powdered litharge. The colour of the solution rapidly disappears, and heat is developed. On distilling off the ether, and exhausting the residue with hot benzene, the iodoricin separates in the crystalline state on cooling. When pure, it forms colourless prisms which melt at 86.5° and decompose, with evolution of violet vapours of iodine, when heated. It is only slightly soluble in cold water, but dissolves readily in hot water, the substance undergoing decomposition when the solution is boiled. It is very soluble in ether and alcohol, moderately so in benzene and in hot petroleum, slightly in carbon sulphide. It is quite destitute of the peculiar astringent sweet taste so characteristic of pure orcin. Mercuric oxide may be employed instead of lead oxide in its preparation, but, from the solubility of mercuric iodide in most liquids, it is not so advantageous (Stenhouse, *Proc. Roy. Soc.* xxii. 53).

**Trinitro-orcinic acid**,  $C^6H^3(NO^2)^3O^2$  (Stenhouse, *Proc. Roy. Soc.* xix. 410). Orcin treated with nitric acid at ordinary temperatures yields nothing but resinous uncrystallisable substances and ultimately oxalic acid; but by proceeding in the following manner, a crystalline nitro-compound may be obtained.

Colourless orcin, prepared from ordinary orcin by distillation in a vacuum, is dissolved in a small quantity of water, and this solution is gradually added to strong nitric acid, cooled to -10°. The pale brown solution thus obtained is now added, with constant stirring, to concentrated sulphuric acid, also maintained at -10°, and the resulting pasty mass, after remaining in the freezing mixture for fifteen or twenty minutes, is poured into a mixture of water and crushed ice; the crude nitro-orcin is thus precipitated as an orange-coloured granular powder amounting to 150 p.c. of the weight of the orcin.

One or two recrystallisations from boiling water render the nitro-orcin pure. It then forms large yellow needles having the composition above stated, readily soluble in hot water, but slightly in cold, and still less so in dilute acids. It is soluble in alcohol, very soluble in hot benzene, and crystallises out in great part on cooling; less soluble in ether, and but moderately so in carbon sulphide. It dyes the skin yellow like picric acid, but is tasteless. It volatilises slightly at 100°, melts at 162°, and decomposes with slight explosion immediately afterwards. When heated with concentrated sulphuric acid, it dissolves, forming a deep yellow solution, which deposits crystals on cooling, and is immediately precipitated by water. It dissolves in hot, strong nitric acid, with evolution of nitrous fumes and formation of oxalic acid. It yields chloropicrin when treated with calcium hypochlorite at the ordinary temperature. Its aqueous solutions are coloured dark brown by ferric chloride, and completely precipitated by lead subacetate. It is a powerful acid much resembling picric acid.

The **potassium salt**,  $C^6H^2(NO^2)^3 \begin{matrix} \diagup O \\ \diagdown O \end{matrix} K^1$ , prepared from potassium carbonate and trinitro-orcinic acid, is very soluble in hot water, and crystallises in needles of a deep orange colour. The **sodium salt**, like the potassium salt, forms orange-coloured needles; the **ammonium salt** forms deep yellow silky needles, which are very soluble in water, but much less so in alcohol. The **barium salt**,  $C^6H^2(NO^2)^3 \begin{matrix} \diagup O \\ \diagdown O \end{matrix} Ba^2 + 3H^2O$ ,

prepared by neutralising a boiling solution of 1 part of nitro-orein in 500 of water with barium carbonate, forms bright yellow needles, which lose their water of crystallisation at  $100^{\circ}$ , and become orange-red. The *calcium salt* forms yellow needles which are very soluble in hot water. The *magnesium salt* is very soluble in cold water, and crystallises in minute orange needles. The *lead salt*,  $\text{C}^{\text{H}}(\text{NO}^2)^3\text{Pb}\text{O}_2$ , prepared by precipitating a very dilute aqueous solution of nitro-oreinic acid with an acidulated solution of lead acetate, forms tufts of microscopic needles, which are almost insoluble in cold water, slightly in hot. It crystallises unaltered from acetic acid. The *copper salt* is very soluble in water and alcohol, and crystallises in reddish-brown needles; the *zinc salt* forms tufts of yellow needles, which are likewise very soluble. The *silver salt*,  $\text{C}^{\text{H}}(\text{NO}^2)^3\text{Ag}_2\text{O}_2$ , prepared from the acid and silver oxide, forms an orange-red, gelatinous mass, which exhibits no signs of crystallisation. It is slowly decomposed by long boiling.

*Ethyl trinitro-oreinate*,  $\text{C}^{\text{H}}(\text{NO}^2)^3\text{(C}^2\text{H}_5\text{)}\text{O}_2$ , prepared by boiling the silver salt with excess of ethyl iodide, crystallises from alcohol in bright yellow prismatic needles, which melt at  $61.5^{\circ}$ . *Methyl trinitro-oreinate* very closely resembles the ethyl compound, but melts at  $69.5^{\circ}$ .

**Amidorecins** (Stenhouse, *Proc. Roy. Soc.* xxi. 122).—*Amido-diimido-orein*,  $\text{C}^{\text{H}}(\text{NH}^2)(\text{NH})\text{O}_2$ .—This base is produced by the oxidation of the triamido-orein prepared by the action of reducing agents, such as sodium-amalgam, tin and hydrochloric acid, or zinc and an acid, on trinitro-orein. It is better, however, to treat trinitro-orein, suspended in water, with sodium-amalgam in a closed vessel until the solution becomes colourless, then to oxidise the clear solution by agitating it with air until it assumes a brilliant blue colour; and finally to precipitate the amido-diimido-orein thus formed as hydrochloride by the addition of an excess of strong hydrochloric acid. On treating the hydrochloride with a slight excess of dilute ammonia, it is decomposed, leaving the free base in an impure state. This is dissolved in warm dilute acetic acid, filtered, and precipitated by a slight excess of ammonia. Two or three solutions and reprecipitations suffice to render it pure, when it forms small needles, having a deep green metallic lustre by reflected light. They are insoluble in most liquids; a solution of sodium hydrate, however, dissolves them with a fine deep blue colour. Treatment with sodium-amalgam reconverts them into triamido-orein.

The *hydrochloride*,  $[\text{C}^{\text{H}}(\text{NH}^2)(\text{NH})\text{O}_2]\text{HCl}$ , crystallises, according to circumstances, either in long silky needles of a brownish-red colour, in rhomboidal plates, or in dark-red thick prisms. It is insoluble in alcohol and ether, moderately soluble in cold, and easily in boiling water, but is at the same time partially decomposed. The *sulphate*,  $[\text{C}^{\text{H}}(\text{NH}^2)(\text{NH})\text{O}_2]^2\text{SO}_4 + \text{H}_2\text{O}$ , forms minute lustrous plates, which are purple by reflected light, and much less soluble in water than the hydrochloride. The *nitrate* closely resembles the sulphate in appearance, but is much more soluble in water. The *oxalate* is obtained in very slightly soluble purple scales, and the *picrate* in iridescent green needles and plates, which are insoluble in alcohol and almost insoluble in water. The *acetate*, which is very soluble in cold water and does not crystallise well, is prepared by dissolving the free base in acetic acid. As the aqueous solutions of the amido-diimido-orein salts are decomposed under the influence of heat, it is best to prepare them by adding the corresponding acid to a solution of the acetate.

*Triamido-orein*.—On boiling trinitro-orein with tin and hydrochloric acid until it becomes colourless, separating the tin by hydrogen sulphide, and evaporating the solution in a vacuum, long colourless needles of triamido-orein hydrochloride are obtained, but owing to their great solubility and the readiness with which they absorb water and deliquesce, the salt has not been obtained in a state fit for analysis. On passing a current of sulphuretted hydrogen through a solution of ammonium sulphhydrate in which amido-diimido-orein is suspended, the latter rapidly loses its colour and becomes converted into a sandy deposit consisting of colourless crystals. These are apparently triamido-orein, and on exposure to the air rapidly acquire a metallic green lustre and become converted into amido-diimido-orein. They also dissolve in hydrochloric acid, the solution acquiring a deep red colour and depositing crystals of amido-diimido-orein when exposed to the air.

**O'RILEYITE.** This is a native arsenite from Burmah, described by D. Waldo (*Chem. News*, xliii. 19). It is steel-grey with metallic lustre on the fresh surface, black and earthy on tarnished faces. Hardness = 5.3. Sp. gr. = 7.243 to 7.423.



Analysis A shows the complete composition, B the mean of two determinations of the chief constituents:

Cu	Fe	As	Sb	X*	Y†
12.13	43.12	38.45	0.54	0.12	6.19 = 100.55
13.28	43.88	37.03			

\* Earthy admixtures.—† Dissolved after 12 hours' digestion with dilute sulphuric acid, and consisting of 1.21 CaO, 1.97 FeO, 1.89 PbO, and 1.12 As<sup>2</sup>O<sub>3</sub>.

**ORTHOCLASE.** See FELSPAR (p. 508).

**OSSEIN.** *Bone Cartilage* (i. 619).—In the organic matter of fossil bones, A. Scheurer-Kestner (*Compt. rend.* lxx. 1179; further, *J. Pharm.* [4], xvii. 111) distinguishes a soluble and an insoluble ossein. The latter is not dissolved by weak hydrochloric acid containing only 0.5 p.c. HCl, but is dissolved by stronger acid. Treated with acid of this strength, a mammoth-bone yielded 63.7 p.c. insoluble and 36.3 soluble ossein, and the bone of *Ursus spelæus* yielded 37.4 insoluble and 62.6 soluble ossein. The soluble ossein exists ready formed in fossil bones, and is not formed—at least not altogether—by the action of the hydrochloric acid on ordinary ossein.

**OXALIC ACID,** C<sup>2</sup>H<sup>2</sup>O<sup>4</sup>. *Formation.*—According to Bertholot (*Compt. rend.* lxx. 256) charcoal (from spindle-tree wood) is attacked by solution of chromic acid, yielding a small quantity of oxalic acid. According to Wippermann (*Deut. Chem. Ges. Ber.* iii. 337) oxalic acid is found amongst the products of the action of ethyl dibromacetate on the mixture of sodacetic ethers obtained by Frankland and Duppa. According to Carius the formation of oxalic acid under these circumstances is due to the decomposition of the ethyl dibromacetate by the sodium ethylate which is likewise present.

*Recovery from the Residues of the 'Discharge' process.*—When cloth which is in parts impregnated with tartaric or oxalic acid, or both, is passed through the discharge-vat, which contains chloride of lime with a greater or smaller excess of lime, decomposition takes place, and the acids are converted into their calcium salts, which, being insoluble, settle, together with the excess of undissolved lime, at the bottom of the vat. If the slimy deposit so produced is allowed to remain in the working vat for some weeks, with frequent agitation, it becomes continually richer in the salts and poorer in free lime, till it attains even such a percentage of the former as 65.5 p.c. calcium tartrate, and 18 p.c. calcium oxalate.

From this mixture, washed and somewhat diluted with water, the acids are liberated by addition of a previously determined quantity of sulphuric acid of 1.568 sp. gr., and after stirring and boiling with as much more water as is equal to the weight of the original deposit, the liquid is separated from the calcium sulphate by means of a centrifugal machine. Any excess of sulphuric acid contained in the liquid is removed by boiling with barium tartrate.

This method affords still better results when chloride of soda (Eau de Labarraque) is employed in the discharging vat in place of the chloride of lime. As the tartrate and oxalate of sodium remain in solution, it is only necessary to add from time to time a sufficient quantity of chloride of lime solution to precipitate all the tartaric and oxalic acids as lime salts, and to restore the original working strength of the vat. In this case the precipitate will contain no calcium hydrate or carbonate, and consequently a great saving of sulphuric acid will be effected.

A further advantage is found to follow the use of the soda-solution, namely, that the whites are whiter, and the reds are less injured, than when the chloride of lime is employed (A. Müller, *Chem. Centr.* 1871, 134).

*Reactions.*—According to G. Bizio (*Zeitschr. f. Chem.* vi. 52) oxalic acid in very dilute solution is oxidised by the oxygen of the air, in shorter or longer time according to the temperature; but in more concentrated solutions this oxidation does not take place.

According to P. Carles (*Compt. rend.* lxxi. 226) when a stream of pure oxygen is passed through a strong solution of oxalic acid, no carbonic acid is formed at ordinary temperatures; but if the oxalic acid be heated to 100°, and oxygen, hydrogen, or nitrogen passed through it, the gas which passes off precipitates barium carbonate from baryta-water, and reduces silver solution. Carles infers from this that the oxalic acid is split up into carbon dioxide and formic acid, and thinks that Bizio's result may be explained in a similar manner.

**Oxalates.** The following table of the solubility of oxalic acid and several metallic oxalates in water is given by W. R. Nichols (*Chem. News*, xxii. 14).

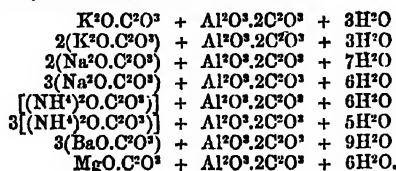
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## Solubility of Oxalates.

	Tempera- ture	Quantity of water required to dissolve 1 part of salt
Oxalic acid, $C^2H^2O^4 + 2H^2O$	14° 5	10·46
Neutral sodium oxalate, $C^2Na^2O^4$	13	31·60
Acid sodium oxalate, $C^2NaHO^4 + H^2O$	10	67·57
Neutral potassium oxalate, $C^2K^2O^4 + H^2O$	16	3·03
Acid potassium oxalate, $4C^2HKO^4 + H^2O$	8	26·21
Potassium quadroxalate, $C^2HKO^4.C^2H^2O^4 + 2H^2O$	13	55·25
Neutral ammonium oxalate, $C^2(NH^4)O^4 + H^2O$	15	23·69
Acid ammonium oxalate, $2C^2(NH^4)HO^4 + H^2O$	11·5	15·97
Ammonium quadroxalate, $C^2(NH^4)HO^4.C^2H^2O^4 + 2H^2O$	7·75	39·68

*Aluminium oxalates.*—The following double oxalates of aluminium have been prepared by A. Z. Collin (*Deut. Chem. Ges. Ber.* ii. 315):—



*Antimony oxalates.*—The following are described by N. Svenssen (*Deut. Chem. Ges. Ber.* iii. 314):—

- (1).  $Sb^2O^3.2C^2O^3 + H^2O$
- (2).  $K^2O.C^2O^3 + Sb^2O^3.3C^2O^3 + H^2O$
- (3).  $3(K^2O.C^2O^3) + Sb^2O^3.3C^2O^3 + 6H^2O$
- (4).  $K^2O.C^2O^3 + Sb^2O^3.3C^2O^3 + K^2O.H^2O.2C^2O^3 + 3H^2O$
- (5).  $3(K^2O.C^2O^3) + Sb^2O^3.3C^2O^3 + 2(K^2O.H^2O.2C^2O^3) + 5H^2O$
- (6).  $3(Na^2O.C^2O^3) + Sb^2O^3.3C^2O^3 + 9H^2O$
- (7).  $(NH^4)^2O.C^2O^3 + Sb^2O^3.3C^2O^3 + 10H^2O$
- (8).  $3[(NH^4)^2O.C^2O^3] + 2(Sb^2O^3.3C^2O^3) + 16H^2O$
- (9).  $3[(NH^4)^2O.C^2O^3] + Sb^2O^3.3C^2O^3 + (NH^4)^2O.H^2O.2C^2O^3 + 15H^2O$

The salt (5) was deposited from the mother-liquors of (3) and (4), for the preparation of which acid potassium oxalate was mixed with antimonious oxide and caustic potash. The salt (4) forms large well-defined crystals. The salt (2) is decomposed by water; so likewise is (8), which was obtained but once. The salts (5) and (9) may be recrystallised from water without alteration.

*Bismuth-potassium oxalate*,  $K^2O.C^2O^3 + Bi^2O^3.3C^2O^3 + 2H^2O$  (Svenssen).

*Cerous oxalate*,  $C^2CeO^4$ , in the air-dried state contains 4 mols. water; after drying at 100° only 1 mol., and this is given off at a higher temperature, partial decomposition, however, taking place at 180°. The air-dried salt gives off 3 p.c. water over sulphuric acid (Erk, *Zeitschr. f. Chem.* vii. 100).

*Lead oxalate*,  $C^2PbO^4$ .—Experiments on the calcination of this salt have been made by E. J. Maumené (*Compt. rend.* lxxi. 797, 837).

The black product left on calcining lead oxalate was considered by Berzelius, and after him by Dulong, to be a suboxide of lead. Subsequently Boussingault found that on exposing this body in a muffle to an incipient red heat, it experienced a gain in weight corresponding with the difference between  $Pb^2O$  and  $2PbO$ . Lastly, its formation and properties were examined by Pelouze, who found, on keeping the oxalate at a temperature of 310°, at which it begins to decompose, that the gases disengaged are carbon monoxide and carbon dioxide in the ratio of  $1CO : 3CO^2$ , according to the equation  $2C^2O^4Pb = Pb^2O + CO + 3CO^2$ .

Maumené, however, finds: 1. That the black residue is a mixture of metallic lead with the monoxide  $PbO$ , inasmuch as, when triturated with mercury for a considerable time—or for a shorter time if previously moistened with alcohol—it yields an amalgam of lead, and when boiled with a solution of sugar it gives up a considerable quantity of lead oxide.

2. That the proportions of carbon monoxide and dioxide evolved in the decomposition are not constant, but vary according to the temperature and other conditions of the experiment. When the oxalate was heated in an oil-bath to  $310^{\circ}$ – $315^{\circ}$ , the gas collected in the early stages of the decomposition exhibited nearly the ratio 1CO; 2CO $^2$ ; but on collecting successive portions of the gas evolved at  $315^{\circ}$ , the proportion of carbon dioxide was found gradually to increase, till at length the evolved gas consisted almost wholly of that compound. This result is due to the gradual oxidation of the carbon monoxide by the lead oxide in the residue. Similar results were obtained at higher temperatures. By calcining a small quantity of the oxalate (1 gram) in a narrow gas tube, of which it occupied a considerable length, and using a regulated flame, a gaseous mixture was obtained exhibiting very nearly the ratio 1CO : 3CO $^2$  mentioned by Pelouze.

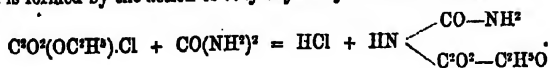
**Oxalylo ethers.** On the action of Sodium on Ethyl oxalate, see GLYCOLLIC ACID (p. 569); also Eghis (*Deut. Chem. Ges. Ber.* iv. 580; *Chem. Soc. J.* [2], ix. 820).

Perfectly dry ethyl oxalate, treated with phosphorus oxychloride, forms ethyloxy-oxalylochloride, COCl–CO(OC $^2$ H $^3$ ), which is a colourless mobile liquid having a suffocating odour, a sp. gr. of 1.2160 at  $16^{\circ}$ , and boiling at  $140^{\circ}$ . It fumes strongly in the air, and when exposed to the air for some time is converted into oxalic acid. With water it decomposes very rapidly; with alcohol it instantly forms ethyl oxalate; with alcoholic ammonia it yields ethyl oxamate; and with aniline ethylic phenyloxamate (L. Henry, *Deut. Chem. Ges. Ber.* iv. 598).

When ethyl oxalate is digested with isopropyl iodide and zinc, first at ordinary temperatures and afterwards at  $100^{\circ}$ , the ethylic ethers of oxy-isocaproic acid and oxy-isovaleric acid (p. 885) are produced, together with a third ethylic ether, which is obtained by heating the lower boiling portion of the crude product with baryta-water to  $100^{\circ}$ , removing the excess of baryta with sulphuric acid, and concentrating the solution. The ether in question then separates in needle-shaped crystals, coloured by iodine. The free acid forms white crystals easily soluble in water, sublimes below  $100^{\circ}$  in white needles, melts at  $91^{\circ}$ – $92^{\circ}$ , and solidifies at  $85^{\circ}$ . This ether is perhaps the isopropyl-compound,  $\begin{matrix} C^3H^7 \\ C^3H^7O \end{matrix} \left\{ \begin{matrix} CO-NH^2 \\ CO^2-OC^3H^7 \end{matrix} \right\} CH_3CO^2H$ , analogous to Frankland & Duppa's amyl-ethyl-hydroxalic acid (iv. 276).

**Action of Oxalic acid on Polyatomic alcohols.**—Oxalic acid forms with glycerin a compound called Oxalin, a white solid hygroscopic substance which, when heated, melts, gives off vapours, and decomposes, evolving carbon dioxide and leaving glycerin. With ammonia it forms oxamide. Similar compounds are formed with mannite, dulcitate, erythrite, quercite, ethene glycol, and octene glycol (Lorin, *Compt. rend.* lxxvii. 329, 363; *Ann. Chim. Phys.* [4], xxix. 367).

**OXALURIC ACID**,  $C^3H^3N^2O^4 = \begin{matrix} CO-NH^2 \\ CO^2-OC^3H^3 \end{matrix} \left\{ \begin{matrix} NH \\ NH \end{matrix} \right\}$ . The ethylic ether of this acid is formed by the action of ethyloxy-oxalyl chloride on urea:—



The action takes place at ordinary temperatures; it is very energetic, and accompanied by considerable evolution of heat. As the hydrochloric acid formed unites with the urea, it is necessary to use a double quantity of the latter. The product is exhausted with cold water, and the residual ethyl oxalurate is recrystallised from boiling water.

Ethyl oxalurate separates from water in thin, white, silky, anhydrous needles; from alcohol as a white crystalline powder.

**OXAMIC ETHERS.** On the formation of these ethers by the action of ammonia and amines on ethyloxy-oxalyl chloride, see above.

**OXAMIDONAPHTHOL.** See NAPHTHOLS (p. 842).

**OXAMIDITE.** This name is given by C. U. Shepard (*Sill. Am. J.* [2], i. 272) to ammonium oxalate found in the vertebral column and the stomach of a bird buried in guano.

**OXIDATION.** On the Heat developed in Oxidation, see HEAT (pp. 606–618).

Lecture experiments on alternate Oxidation and Reduction are described by A. W. Hofmann (*Deut. Chem. Ges. Ber.* iii. 658), and by J. Thomsen (*ibid.* 930); see also *Jahresb. f. Chem.* 1870, 197; also by Wartha (*Deut. Chem. Ges. Ber.* iv. 94; *Jahresb.* 1871, 197).

On Oxidation in the Animal Organism, see Pfüger (*Pfüger's Archiv. f. Phys.* vi. 43; *Chem. Soc. J.* [2], x. 1030).

On the Oxidising Power of the Blood, see p. 200 of this volume; on the Influence of Quinine on the Oxidation in the Blood, see p. 197.

**OXIDES.** On the alleged Influence of Calcination on the Heat disengaged in the Solution and certain Reactions of Metallic Oxides, see p. 617.

On the Effect of various metallic Oxides in facilitating the Decomposition of Potassium Chlorate by Heat, see p. 315.

**OXIMIDO-HYDROXYL-ANTHRAQUINONE.** See ANTHRAQUINONE (p. 91).

**OXIMIDONAPHTHOL.** See NAPHTHOL (p. 812).

**OXINDOL.** See INDIGO (p. 666).

**OXYAZOBENZENE.** See BENZENE (p. 151).

**OXYANTHRAQUINONE.** See ANTHRAQUINONE (p. 92).

**OXYBENZOIC ACID.** On the relative positions of the radicles OH and COOH in this acid and its isomerides, see BENZENE (p. 133).

**OXYBUTYRIC ACIDS,**  $C^4H^3O^3 = C^4H^2(OH)O^2$  (Markownikoff, *Ann. Ch. Pharm.* cliii. 228, 251; *Zeitschr. f. Chem.* iv. 620; vi. 421). The following observations on these acids are supplementary to those reported in the 1st *Suppl.* (p. 891).

(1). *Theoryisobutyric acid*,  $\begin{matrix} H^3C \\ H^2C \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} \begin{matrix} COH \\ COOH \end{matrix}$  — COOH, formed from bromisobutyric

acid, is a white crystalline body easily soluble in water, and separates from the aqueous solution over sulphuric acid in prismatic crystals, from ether in stellate groups of needles. When continuously heated it sublimates at  $50^\circ$  in slender flexible needles, which melt at  $79^\circ$  and resolidify at  $76^\circ$ . It absorbs moisture from the air. The *ammonium salt* is very soluble. The *calcium salt* crystallises in spherical groups of slender needles having a silky lustre. Alcohol throws it down from its aqueous solution as a gelatinous precipitate which dissolves when heated, but separates in needles on cooling. The *barium salt* dissolves easily in hot water and in hot alcohol, and crystallises in prisms. The *zinc salt* dissolves sparingly both in hot and in cold water, and separates on evaporation by heat in microscopic six-sided laminae, on spontaneous evaporation in four-sided plates. It contains 2 mol. water of crystallisation. The *lead salt* is very soluble. The *silver salt* crystallises from hot aqueous solution in shining scales, by slow evaporation in large flat prisms. It dissolves in 14 parts of water.

Oxyisobutyric acid is converted by oxidation with potassium dichromate and sulphuric acid into carbon dioxide, acetone, and acetic acid. According to Markownikoff, it is identical with acetic acid, dimethoxalic acid, and butylactic acid.

(2).  *$\alpha$ -Oxybutyric acid* is prepared from chlorinated or brominated butyl chloride in the same manner as oxyisobutyric acid. This acid, represented by the formula  $CH^3.CH^2.CHOH.CO^2H$ , is identical with that which Friedel and Machuca obtained from bromobutyric acid (1st *Suppl.* 891). It crystallises from aqueous solution over sulphuric acid in stellate groups of needles; from solution in aqueous ether in small flat prisms. It deliquesces in moist air, melts at  $43^\circ$ – $44^\circ$ , sublimates below  $100^\circ$ , and begins to boil, with incipient decomposition, at  $225^\circ$ . The *calcium salt*,  $2Ca(C^4H^3O^3)^2 + 6H^2O$ , is easily soluble in water, and crystallises in nodular masses. The *zinc salt*,  $Zn(C^4H^3O^3)^2 + H^2O$ , crystallises from hot aqueous solution in nodular aggregates consisting of slender four-sided prisms united in tufts; by slow crystallisation it is obtained in long needles. The *lead salt* and the *silver salt* are easily soluble in water, the latter crystallising therefrom in druses.

(3).  *$\beta$ -Oxybutyric acid*,  $CH^3.CH(OH).CH^2.COOH$ , prepared from propylene-chlorhydrin, has already been described (1st *Suppl.* 301).

**OXYCAMPHORIC ANHYDRIDE,**  $C^{10}H^{14}O^4$ . See CAMPHORIC ACID (p. 236).

**OXYCAMPHORONIC ACID,**  $C^{10}H^{12}O^4$ . See CAMPHORONIC ACID (p. 238).

**OXYCARBONS or CARBON OXIDES.** Two of these bodies,  $C^2O^2$  and  $C^2O^4$ , analogous to the hydrocarbons, crotonylene  $C^4H^2$ , and valerylone  $C^5H^2$ , have been obtained, together with others of undetermined composition, by exposing pure dry carbon monoxide to the action of electricity in an induction tube (Brodie, p. 350).

**OXYCUMIC ACID,**  $C^8H^4.C^2H^2OH.CO^2H$ , and **OXYTETRACUMIC ACID,**  $C^8H^4.C^2H^2O^2CH^2.CO^2H$ , are formed, together with other compounds, by boiling bromocumic acid with alcoholic potash (p. 403). The former yields a *barium salt* which crystallises in nodules (Czempelik).

**OXYGEN.** *Preparation.*—A process for obtaining oxygen from atmospheric air for industrial use, founded on the property possessed by water, of absorbing oxygen more readily than nitrogen, has been devised by Mallet (*Dingl. pol. J.* exxcix. 112). Air is pressed into water by means of a forcing-pump, and the gases which escape on diminishing the pressure are subjected to the same treatment eight times in succession, by which time nearly pure oxygen is obtained. The following table shows the composition of the gaseous mixture at each successive stage.

Atmospheric air			Composition after successive pressures							
			1	2	3	4	5	6	7	8
N	.	79	66·67	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O	.	21	33·33	47·5	62·5	75·0	85·0	91·0	95·0	97·3

The difficulty of obtaining oxygen free from nitrogen arises, according to Houzeau (*Compt. rend.* lxx. 39), from the adhesion of atmospheric air to the surface of the glass, which is so strong that the air cannot be completely removed even by washing with large quantities of oxygen. The difficulty may, however, be overcome by keeping the glass-red-hot while a strong stream of oxygen is passed over it. The oxygen is evolved from fused potassium chlorate in retorts heated over their entire surface, and containing ignited asbestos in their necks.

On the influence of various metallic oxides in facilitating the evolution of oxygen from potassium chlorate, see CHLORATES, p. 315; also G. Krebs (*Zeitschr. f. Chem.* vi. 243; *Jahresb. f. Chem.* 1870, 208).

Experiments on the effect of dilution on the oxidising power of oxygen have been made by W. Müller (*Pogg. Ann.* cxli. 95). In the case of iron, copper, and arsenic, oxidation was found to commence in atmospheric air at a lower temperature than in pure oxygen, whereas in the case of charcoal, sulphur, antimony, potassium, iron sulphide, and lead, no difference in the temperatures of commencing oxidation was observed.

**OXYHYDROMUCONIC ACID.** See MUCONIC ACID (p. 827).

**OXYISOBUTYRIC ACID.** See OXYBUTYRIC ACID (p. 884).

**OXYISOCAPRYLIC ACID,**  $C^8H^{14}O^2 = \begin{smallmatrix} C^8H^7 \\ C^8H^7 \end{smallmatrix} COH.CO^8H$  (Markownikoff, *Zeitschr. f. Chem.* vi. 516). The *ethylis ether* of this acid,  $C^8H^{13}(C^8H^4)O^2$ , is prepared by digesting rather more than 2 mol. isopropyl iodide with 1 mol. ethyl oxalate and zinc for some days at the ordinary temperature; the mixture is then diluted with water, mixed with hydrochloric acid to remove the zinc, and then distilled as long as drops of oil continue to pass over. The portion of the oily distillate which goes over between 180° and 205° is boiled for six hours with a weak solution of potash, after which the ether, when fractionally distilled, passes over for the most part between 198° and 200°. It is a thick pale yellow liquid having a faint mouldy smell, boiling at 202°–204° (corr.). It is not saponified by caustic potash at 180°, but baryta at 160° saponifies it slowly.

Oxyisocaprylic acid is best obtained by heating the ether with alcoholic potash. After the alcohol has been distilled off, the residue solidifies on addition of hydrochloric acid to a pasty mass, from which it may be obtained by recrystallisation from water, in slender colourless needles. By spontaneous evaporation longer needles are obtained and sometimes rather large transparent flat prisms. It dissolves sparingly in cold water, easily in alcohol and ether; melts under water, and volatilises with aqueous vapour. It melts at 110°–111°, and then often remains liquid below 80°. When heated above its melting point it sublimes in long needles.

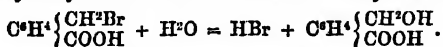
*Barium Oxyisocaprylate*,  $Ba(C^8H^{13}O^2)^2 + 3H^2O$ , crystallises from hot water in small prismatic needles which appear to effloresce easily. The *calcium salt* is easily soluble in water, and crystallises with difficulty. The *zinc salt* separates as an amorphous precipitate on heating the *ammonium salt* with zinc sulphate.

**OXY-ISOVALERIC ACID,** or *Pseudo-propyl-hydroxalic acid*,  $C^8H^{14}O^3 = C^8H^7.CO^8H.CO^8H.CO^8H$  (Markownikoff, *loc. cit.*) This acid is obtained, on evaporating the potash-solution used in the preparation of crude oxyisocaprylic acid, then acidulating with sulphuric acid, agitating with ether, and evaporating the ethereal solution, as a

thick liquid which solidifies in the exsiccator. It appears to be identical with the acid which Fittig & Clarke obtained from bromovaleric acid. The *barium salt*,  $\text{Ba}(\text{C}^3\text{H}^4\text{O}^3)^2$ , which is anhydrous, is best obtained by precipitating its aqueous solution with hot strong alcohol. The aqueous solution, when concentrated by heat, leaves it in the form of a syrup; by spontaneous evaporation, it yields crystalline nodules. The *silver salt*,  $\text{AgC}^3\text{H}^4\text{O}^3$ , is slightly soluble in cold water, rather more soluble in hot water, from which it crystallises in dendrites. The *zinc salt* is a white flocculent precipitate but slightly soluble in water, either hot or cold.

**OXYLEPIDENE**,  $\text{C}^3\text{H}^4\text{O}^3$ . See **LEPIDENE** (p. 773).

**OXYMETHYL-PHENYL-FORMIC ACID**,  $\text{C}^8\text{H}^8\text{O}^3 = \text{C}^8\text{H}^7\left\{\begin{smallmatrix} \text{CH}_2\text{OH} \\ \text{COOH} \end{smallmatrix}\right.$  (Dittmar & Kekulé, *Deut. Chem. Ges. Ber.* iii. 894). This acid is formed by heating 1 mol. of ordinary toluic acid to  $160^\circ$ – $170^\circ$  in a long-necked flask, and slowly drawing 1 mol. bromine-vapour through the apparatus by means of an aspirator. A brominated toluic acid is thereby formed having its bromine in the methyl, and capable of exchanging it for hydroxyl when boiled with alkalis or baryta-water:



The oxyacid forms white plates or smooth needles, very soluble in hot, moderately in cold water. It melts at a temperature somewhat higher than toluic acid and sublimes in feathery groups of needles.

**OXYNAPHTHAQUINONE**. See **NAPHTHAQUINONES** (p. 836).

**OXYNEURINE**. This base, produced by the action of trimethylamine on monochloroacetic acid, is identical with betaine from beet-juice (p. 186).

**OXYPICRIC** or **STYPHENIC ACID**,  $\text{C}^6\text{H}^3(\text{NO}^2)_3\text{O}^2$ , is identical with trinitroresorcin (see **RESORCIN**).

**OXYPYROTARTARIC ACID**,  $\text{C}^4\text{H}^4\text{O}^5 = \text{C}^4\text{H}^3(\text{OH})(\text{COOH})^2$ . This bibasic acid, homologous with malic acid, was obtained by Maxwell Simpson (*Proc. Roy. Soc.* xiii. 44), by heating dichlorhydrin with potassium cyanide in alcoholic solution, and boiling the product with potash. An acid apparently identical with this is produced by the action of melting potassium hydrate on either of the three sulphopyrotartaric acids formed by the combination of sulphurous acid (sulphites of alkali-metal) with citraconic, itaconic, or mesaconic acid. The oxypyrotartaric acid thus obtained forms hard crystals very soluble in cold water, slightly soluble in alcohol and in ether. From a neutralised solution it is precipitated bluish-white by cupric salts. The *silver salt*,  $\text{C}^4\text{H}^3\text{Ag}^2\text{O}^5 + \text{H}_2\text{O}$ , gives off its water of crystallisation at  $65^\circ$  and decomposes at  $100^\circ$  (Wieland, *Ann. Ch. Pharm.* clvii. 34).

**OXSALICYLIC ACID**,  $\text{C}^7\text{H}^4\text{O}^4$ . According to Liechti (*Zeitschr. f. Chem.* vi. 193), this acid prepared by Lautemann's process (decomposition of iodosalicylic acid by potash) is not identical with hypogallic acid, inasmuch as it cannot be made to unite with water of crystallisation, whereas hypogallic acid crystallises with  $1\frac{1}{2}$  mol. water (148 p.c.), which it gives off at  $100^\circ$  (see further **SALICYLIC ACID**, 1st *Suppl.* 1005).

**OXSULPHAZOTATES**. See **SULPHAZOTIC ACIDS**.

**OXSULPHIDE OF CARBON**, COS. See **CARBON OXSULPHIDE** (p. 262).

**OXSULPHOBENZIDE**,  $\text{C}^7\text{H}^5\text{SO}^2 = (\text{C}^6\text{H}^4\text{OH})^2\text{SO}^2$ . This compound, discovered by Glutz (1st *Suppl.* 894), has been further examined by Annaheim (*J. pr. Chem.* [2], i. 14; ii. 385). It is best prepared by heating equal weights of phenol and strong sulphuric acid to  $190^\circ$ – $195^\circ$  for five or six hours, and pouring the mass into two or three times its volume of water.

*Ethyl-oxysulphobenzide*,  $(\text{C}^6\text{H}^4\text{OC}^2\text{H}^5)^2\text{SO}^2$ , is formed by treating oxysulphobenzide with ethyl iodide and alcoholic potash. It is insoluble in water, nearly insoluble in cold alcohol, easily soluble in ether and hot alcohol, and crystallises from the latter in white laminae which melt at  $160^\circ$ . Strong nitric acid converts it into a nitro-product,  $[\text{C}^6\text{H}^4(\text{NO}^2)(\text{OC}^2\text{H}^5)]^2\text{SO}^2$ .

With methyl iodide and amyl iodide oxysulphobenzide yields derivatives of similar character.

*Tetrachloroxysulphobenzide*,  $(\text{C}^6\text{H}^3\text{Cl}^4\text{OH})^2\text{SO}^2$ , is formed, together with other products, by treating oxysulphobenzide with potassium chlorate and hydrochloric acid, and purified by washing it with water and with alcohol, dissolving it in alcohol, and separating by water. It forms short thick prisms or white needle-shaped crystals, insoluble in water, sparingly soluble in cold alcohol, easily in hot alcohol, and in ether, benzene and alkalis. It melts at  $298^\circ$ – $299^\circ$ .

**OXYTOLUIC ACID**,  $C^8H^9O^3$ . Syn. with Oxymethyl-phenyl-formic acid (p. 886).

**OXYTHYMOQUINONE**. See THYMOQUINONES.

**OZONE**. *Formation*.—From numerous experiments on the formation of ozone under the influence of the spark of a Ruhmkorff coil, Houzeau (*Compt. rend.* lxx. 1286) finds that the formation is more rapid in renewed than in confined air, and that it takes place more abundantly at the negative than at the positive pole. The formation of ozone increases with the duration of the electrification up to a certain point only; it increases with the intensity of the electricity; diminishes as the distance between the electrodes is increased; varies with the length or surface of the electrodes; and increases, under otherwise similar circumstances, when the action of both electrodes is made available. Ozone is likewise formed when the electrodes are surrounded through their whole length with thin glass tubes, either closed or open, less abundantly, however, than when the air has free access to the platinum wires. In this case also the quantity of ozone formed varies with the length and surface of the electrodes. The formation of ozone increases considerably as the temperature is lowered, and under otherwise similar circumstances oxygen yields from 7 to 10 times as much ozone as atmospheric air. The ozone produced by electrification of air is contaminated with small quantities of nitrogen-compounds. Guided by these experiments, Houzeau has constructed an apparatus called an 'ozoniser,' by which ozone is produced in considerable quantity.

In an ordinary straight gas-delivery tube is placed a wire of copper, lead, or better, of platinum, 4 to 6 decimeters long, with one of its extremities passing through the side of the upper portion of the tube. On the exterior of the tube is coiled a similar wire over the path of the preceding. When the two are placed in communication with a Ruhmkorff's coil giving a 2 or 3 centimeter spark, a slow stream of oxygen passing through the tube will be strongly charged with ozone. By this apparatus, Houzeau has prepared oxygen containing 60 to 120 (once 188) milligrams of ozone per litre. Electrolysis of water furnished only 3 to 5 milligrams, barium peroxide and sulphuric acid 10 milligrams per litre.

A somewhat similar apparatus is described by A. W. Wright (*Sill. Am. J.* [3], iv. 26; *Chem. Soc. J.* [2], x. 1071).

Boillot (*Compt. rend.* lxxv. 214; *Chem. Soc. J.* [2], x. 879) describes an apparatus consisting of two glass tubes one fitting within the other, and each coated externally with powdered coke made to adhere by means of gelatin. The coatings of the two tubes are connected with the poles of an induction coil, and a stream of oxygen is made to pass between the tubes. The oxygen is thus exposed to the influence of the silent discharge, and a considerable proportion of it is converted into ozone.

On the formation of ozone in rapid combustion, see A. Loew (*1st Suppl.* 894).

On the simultaneous formation of ozone, hydrogen dioxide, and ammonium nitrite by the combustion of hydrogen in the air, see p. 660 of this volume; also C. Thau (*J. pr. Chem.* [2], i. 415; *Chem. Soc. J.* [2], ix. 482).

*Supposed formation of Ozone by the Oxidation of Essential Oils*.—It is commonly stated, on the authority of Schönbein and others, that the oxidation of oil of turpentine, and other essential oils in the air, is attended with formation of ozone, inasmuch as the oxidised oil and the air in its vicinity exhibit the reaction of ozone with potassium iodide (v. 921); this active substance likewise resembles hydrogen dioxide in giving a violet coloration with chromic acid solution, acidulated with sulphuric acid. The nature of this compound has lately been examined by Kingzett (*Chem. Soc. J.* [2], xii. 511), who finds that it cannot be either ozone or hydrogen dioxide, because it is destroyed at the boiling-point of turpentine-oil, viz.  $160^{\circ}$ , at which temperature ozone and hydrogen dioxide are permanent; moreover it resists to a certain extent the action of sodium thiosulphate, and its solution in water retains its properties after long-continued boiling. Kingzett attributes the active properties of the oxidised turpentine-oil to the formation of monohydrated terpene oxide,  $C^{10}H^{14}O.H^2O$ , which was shown some time ago by Sobrero (*Ann. Ch. Pharm.* lxxx. 106) to be formed when turpentine-oil containing water is exposed to the sun's rays in a vessel filled with oxygen (see TURPENTINE-OIL).

*Properties and Reactions*.—According to Carius (*Deut. Chem. Ges. Ber.* v. 520), 1,000 c.c. of distilled water at  $0^{\circ}$  and 0.76 m.m. pressure absorb from 3.86 to 5.41 c.c. of ozone.

According to Jonglet (*Compt. rend.* lxx. 539), nitroglycerin, dynamite, iodide of nitrogen, and chloride of nitrogen explode in a vessel containing ozone. Powder made with potassium picrate decomposes slowly under the same circumstances; ordinary gunpowder alters considerably in the course of six weeks.

On Atmospheric Ozone, see ATMOSPHERE (p. 113).

Gorup-Besanes finds that the air in the neighbourhood of graduation-houses for the evaporation of saline springs, is more highly charged with ozone than ordinary air (*Ann. Ch. Pharm.* clxi. 232; *Chem. Soc. J.* [2], x. 384).

The so-called 'Autozone.'—This supposed modification of oxygen is formed, according to Houzeau (*Jahresb. f. Chem.* 1855, 286), and Schönbein, (*ibid.* 1861, 96), by the action of strong sulphuric acid on barium dioxide; according to Moissner (*ibid.* 1863, 106), simultaneously with ozone, by electrification of oxygen. On the other hand, v. Babo (*ibid.* 1863, 135), and Weltzien (*ibid.* 1866, 106), found that the supposed peculiar modification of oxygen thus produced was nothing but hydrogen dioxide; and this conclusion has lately been confirmed by an elaborate series of experiments made by Engler n. Nasse (*Ann. Ch. Pharm.* cliv. 215; *Jahresb.* 1870, 210).

## P

**PALLADIUM.** On alloys of Palladium and Lead, see LEAD (p. 729).

On Hydrogenised Palladium, see HYDROGEN (p. 658).

**Palladic Chloride, PdCl<sup>4</sup>.** Double salts of this chloride, analogous to those of platonic chloride, have been prepared and examined by H. Topsøe (*Chem. Centr.* 1870, 684). The potassium and ammonium salts are obtained as crystalline precipitates on mixing palladic chloride with potassium or ammonium chloride; the other compounds, which are easily soluble, are obtained by mixing the respective solutions and evaporating over sulphuric acid, taking care that the liquid is always saturated with chlorine. These double salts are very unstable; those of the magnesium series give off chlorine even on keeping or on solution in water, whereas those of the alkali-metals do not decompose till their solutions are heated. They have a crimson colour.

The following have been prepared:—

PdCl <sup>4</sup> .2NH <sup>4</sup> Cl:	Regular. Combination, O.∞O∞. Sp. gr. = 2.418.
PdCl <sup>4</sup> .2KCl:	Regular. Combination, O.∞O∞. Sp. gr. = 2.738.
PdCl <sup>4</sup> .2MgCl <sup>2</sup> + 6H <sup>2</sup> O:	Deliquescent. Hexagonal. Combination, ∞P∞ and R of 127°. Sp. gr. = 2.124.
PdCl <sup>4</sup> .2NiCl <sup>2</sup> + 6H <sup>2</sup> O:	Deliquescent. Hexagonal. Combination, ∞P∞ and R of 127° 14'. Sp. gr. = 2.353.
PdCl <sup>4</sup> .2ZnCl <sup>2</sup> + 6H <sup>2</sup> O:	Isomorphous with the two preceding. R of 127° 10'. Sp. gr. = 2.359.

The analogy of these salts with the platonic double chlorides is exhibited by the following comparison:—

PdCl <sup>4</sup> .2NH <sup>4</sup> Cl . . . . .	147.1	PtCl <sup>4</sup> .2NH <sup>4</sup> Cl . . . . .	148.6
PdCl <sup>4</sup> .2KCl . . . . .	145.3	PtCl <sup>4</sup> .2KCl . . . . .	138.2
PdCl <sup>4</sup> .MgCl <sup>2</sup> + 6H <sup>2</sup> O . . . . .	212.6	PtCl <sup>4</sup> .MgCl <sup>2</sup> + 6H <sup>2</sup> O . . . . .	222.6
PdCl <sup>4</sup> .NiCl <sup>2</sup> + 6H <sup>2</sup> O . . . . .	206.7	PtCl <sup>4</sup> .NiCl <sup>2</sup> + 6H <sup>2</sup> O . . . . .	206.3
PdCl <sup>4</sup> .ZnCl <sup>2</sup> + 6H <sup>2</sup> O . . . . .	208.0	PtCl <sup>4</sup> .ZnCl <sup>2</sup> + 6H <sup>2</sup> O . . . . .	214.8

**Oxides.** When a sulphur-salt of palladium is fused with a mixture of potassium hydrate and nitrate, a dark brown-black powder is formed, consisting of an oxide of palladium, which is reduced to the metallic state by strong and prolonged ignition, and gives up variable quantities of palladium to nitromuriatic acid, leaving an oxide having the composition Pd<sup>2</sup>O<sup>3</sup>, or perhaps 4PdO.PdO<sup>2</sup>. This oxide is not decomposed by nitromuriatic acid, but is easily reduced by hydrogen. When ignited over an ordinary gas-burner it gives off its oxygen but slowly, the reduction being complete only after strong and prolonged ignition. Under the microscope it presents the appearance of a perfectly homogeneous light-brown lustreless powder (R. Schneider, *Pogg. Ann.* cxli. 519).

**Sulphides.** The *bisulphide*, PdS<sup>2</sup>, is formed by decomposing sodium sulphopalladate, Na<sup>2</sup>S.PdS<sup>2</sup> (*infra*) with hydrochloric acid. After drying it forms a dark black-brown rather dense crystalline powder, exhibiting under the microscope the acicular form of the sulphopalladate from which it has been separated. It is permanent in the air. When moderately heated (in carbon dioxide) it yields a considerable



sublimate of sulphur, and is converted first into monosulphide, then at a higher temperature into the hemisulphide. The bisulphide is slowly dissolved by nitric acid, quickly and completely by nitromuriatic acid.

The *hemisulphide*,  $\text{Pd}^2\text{S}$ , is also produced by fusing an intimate mixture of 1 pt. ammonio-palladious chloride (or  $\frac{1}{2}$  pt. palladium monosulphide), 6 pts. of potassium carbonate (or an equivalent quantity of sodium carbonate), 6 pts. of sulphur and 3 pts. of sal-ammoniac, for 15–20 minutes at a bright red-heat. On treating the fused mass with water, and washing away the potassium-palladium sulphopalladate formed at the same time, the hemisulphide remains as a fused regulus. It is rather hard, very brittle, and easily pulverised; the powder is ash-grey. On recent fracture-surfaces it exhibits a rather bright metallic lustre, a whitish-grey colour, and a fine-grained crystalline structure. Sp. gr. = 7.303 at  $15^\circ$ . It is not attacked by acids, and but very slightly even by nitromuriatic acid. At a red-heat it melts slowly, gives off sulphur, but still retains some of that substance even after prolonged ignition. It behaves in the same way when heated in a stream of hydrogen.

*Sulphide or Palladium Sulphopalladate*,  $\text{Pd}^2\text{S}^4$  (see below).

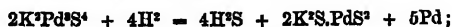
**Sulphopalladates** (R. Schneider, *Pogg. Ann.* cxl. 519; cxlviii. 625; *J. pr. Chem.* [2], iii. 103). *Sodium Sulphopalladate*,  $\text{Na}^2\text{S}.\text{PdS}^2$ , is formed in thin brown needles by fusing 1 pt. of ammonio-palladious chloride (or  $\frac{1}{2}$  pt. palladium monosulphide) with 6 pts. of dry sodium carbonate and 6 pts. of sulphur, and treating the coarsely-pounded fused mass with absolute alcohol (out of contact with the air) till the sodium polysulphide is completely dissolved out. The remainder is a mixture of sodium sulphate with the sulphopalladate,  $\text{Na}^2\text{S}.\text{PdS}^2$ .

This compound forms thin needles partly somewhat flattened, having a brown colour or (especially in the larger specimens) reddish lead-grey on the surface, and a faint metallic lustre. Very thin layers appear translucent with red-brown colour under the microscope. The streak-powder is yellowish-brown. The aqueous solution, when exposed to the air, soon deposits palladium sulphide.

*Silver Sulphopalladate*,  $\text{Ag}^2\text{S}.\text{PdS}^2$ , is formed by adding the sodium salt just described to an alcoholic solution of silver nitrate, diluting with water and stirring, and finally treating the black-brown crystalline powder with aqueous silver nitrate.

*Potassium - palladium Sulphopalladate*,  $\text{K}^2\text{PdS}^4 = \text{K}^2\text{Pd}^2(\text{Pd}^2)^2\text{S}^4 =$   
 $\begin{array}{c} \text{K}-\text{S} \quad \quad \quad \text{S}-\text{Pd} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{Pd} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{K}-\text{S} \quad \quad \quad \text{S}-\text{Pd} \end{array}$  This salt is produced by fusing 2 pts. ammonio-palladious chloride (or 1 pt. of ordinary palladium sulphide) with 12 pts. of potassium carbonate and 12 pts. of sulphur. On treating the fused mass with water, the double sulphur salt remains undissolved, while potassium polysulphide is dissolved, together with potassium sulphopalladate, which has not yet been isolated.

Potassium-palladium sulphopalladate forms very thin six-sided crystalline laminae, having a bright metallic lustre and a splendid blue colour. It is insoluble in water, whether cold or hot. The crystals, heated out of contact with the air, acquire a vortical movement, and at a strong red-heat split with faint sparkling into smaller fragments, without separation of sulphur or of gas. Heated in a stream of hydrogen, they decompose, apparently according to the equation:



and on treating the residue with water, the basic potassium sulphopalladate,  $2\text{K}^2\text{S}.\text{PdS}^2$ , is dissolved.

*Palladium Sulphopalladate*,  $\text{Pd}^2\text{S}^4 = 2\text{PdS}.\text{PdS}^2 = \text{Pd} \begin{array}{c} \diagup \quad \diagdown \\ \text{S} \quad \text{S} \\ \diagdown \quad \diagup \end{array} \text{Pd} \begin{array}{c} \diagup \quad \diagdown \\ \text{S} \quad \text{S} \\ \diagdown \quad \diagup \end{array} \text{Pd}$ ,

is formed by treating potassium-palladium sulphopalladate with hydrochloric acid, the action apparently taking place by two stages, in the first of which the potassium is replaced by hydrogen, yielding the compound,  $\text{H}^2\text{S}.\text{Pd}^2\text{S}.\text{PdS}^2$ , which is then acted upon by atmospheric oxygen in the manner represented by the equation:



The palladium bisulphide in this compound exhibits nearly the same properties as when it is by the free state. By strong ignition in the air half of the sulphur of the bisulphide is driven off in combination with oxygen; and the residue consists of palladium monosulphide, which as thus obtained is a blackish-grey crystalline powder very little acted on by nitromuriatic acid.

**Silver-palladium Sulphopalladate**,  $\text{Ag}^{2\text{S}}_{\text{PdS}}$ .—When two molecules of silver nitrate in dilute aqueous solution are added to one molecule of potassium-palladium sulphopalladate suspended in water, the latter salt loses its blue colour, becomes whitish-grey, and at the same time an amount of potassium nitrate equivalent to that of the silver nitrate used is formed. A new salt is also produced, which, however, contains varying amounts of finely divided metallic silver. But by using a dilute ammoniacal solution of silver nitrate, and treating the product with cold nitric acid for a short time, silver-palladium sulphopalladate is obtained in whitish-grey metallic-looking hexagonal plates having the composition above given. It is characterised by great stability, not being acted on by water, ammonia, potash, or even boiling hydrochloric acid. The residue, after heating out of contact with air, is partially decomposed by boiling nitric or nitromuriatic acid. Heated in the air it absorbs oxygen, the residue when heated with water yielding silver sulphate, but no palladium salt. On heating it in a stream of hydrogen, sulphuretted hydrogen is evolved. Boiling nitric acid removes all the silver and a part of the palladium from the residue, a grey crystalline powder remaining, which is probably palladium subsulphide.

**PALM OIL.** Oudemans (*J. pr. Chem.* [2], ii. 393) has examined the fat of palm kernels, by saponifying it with caustic potash, separating the fatty acids with sulphuric acid, washing with water, and distilling for a long time with water; then—(1) saturating the distillate with baryta and analysing the barium salt; (2) dissolving the residue of the distillation in alcohol, mixing the solution with water, and crystallising out the fatty acids by exposure to a low temperature. Those acids were separated by Heintz's method (iii. 1070). To separate the oleic acid, the soap-solution was precipitated with lead acetate, the air-dried precipitate treated with ether, the acid separated from the ether-solution by hydrochloric acid, and then distilled in a stream of hydrogen. In this manner the following results were obtained:—

Triolein	26.6 p.c.	Trilaurin	
Tristentin		Tricaprin	
Tripalmitin	33.0 p.c.	Tricaprylin	
Trimyristicin		Tricaproin	
			40.4 p.c.

**PAPAVERINE**,  $\text{C}^{21}\text{H}^{21}\text{NO}^4$  (Hesse, *Zeitschr. f. Chem.* vii. 641; *Ann. Ch. Pharm. Suppl.* viii. 261). Respecting the separation of this base from the other alkaloids of opium, see 1st *Suppl.* 896, and p. 876 of this volume.

Papaverine dissolves without colour in strong sulphuric acid, provided that no rise of temperature takes place; but when strong sulphuric acid is poured upon crystals of the base, the heat produced by the reaction is sufficient to give a faint purple colour to the crystals and the solution. With sulphuric acid containing ferric oxide, the coloration is not so strong as with the pure acid. A recently prepared solution of papaverine in sulphuric acid gives, on addition of water, a milky turbidity or a resinous precipitate which is quickly converted into colourless crystals of papaverine sulphate. No other alkaloid of opium exhibits this reaction; the solution of pseudomorphine in strong sulphuric acid also gives a precipitate with water, but it is crystalline. When a solution of papaverine in strong sulphuric acid is heated, it assumes a dark violet colour, and on subsequent addition of water, deposits dark brown amorphous flocks which are nearly insoluble in dilute sulphuric or hydrochloric acid, also in ether, alcohol, and water, but dissolve readily in strong sulphuric acid, potash, and ammonia, with splendid purple-red colour, and are re-precipitated from the ammoniacal solution by acetic acid. The purple-red basic solution possesses great tinctorial power.

**Papaverine hydrochloride**,  $\text{C}^{21}\text{H}^{21}\text{NO}^4.\text{HCl}$ , obtained by saturating the alcoholic solution of the base with hydrochloric acid, forms large prisms having an acid reaction, soluble in 37.3 pts. water at  $18^\circ$ ; when dissolved with aid of heat, it is very apt to form supersaturated solutions.

E. L. Mayer (*Deut. Chem. Ges. Ber.* iv. 128) states that when this salt is treated for a short time with zinc chloride at  $125^\circ$ , it is converted into the salt,  $\text{C}^{21}\text{H}^{20}\text{NO}^4.2\text{HCl}$ , by elimination of 1 mol.  $\text{H}^2\text{O}$  from 2 mol. of the original salt. According to Hesse, however, this supposed new derivative is nothing but papaverine hydrochloride. By prolonged action of zinc chloride, especially at a high temperature, the molecule is decomposed. **Papaverine platino-chloride**,  $2(\text{C}^{21}\text{H}^{21}\text{NO}^4.\text{HCl}).\text{PtCl}_4 + 2\text{H}^2\text{O}$ , is a yellow precipitate made up of small prisms. The *nitrate* forms large prisms. The *acid tartrate* is easily soluble. The *acid oxalate*, formed from oxalic acid and the base, crystallises in white prisms, easily soluble in hot alcohol, sparingly in cold alcohol; 1 pt. dissolves in 388 pts. water at  $10^\circ$ . The base is completely precipitated from its solutions by oxalic acid.

**Nitropapaverine**,  $C^{21}H^{28}(NO^2)NO^4$ , is prepared by heating 1 pt. of papaverine with about 10 pts. nitric acid of sp. gr. 1.06 to the boiling point, decomposing the nitropapaverine nitrate which separates on cooling, with ammonia, dissolving the separated base in hydrochloric acid, precipitating it as sulphate, separating it from this salt by ammonia, and recrystallising from boiling dilute alcohol. During the recrystallisation and drying it must be kept in the dark, as light colours it yellow.

Nitropapaverine generally forms pale yellow prisms, felted together to a woolly mass; better developed prisms are obtained by crystallisation from strong alcohol. When crystallised from dilute alcohol or precipitated by ammonia, it contains 1 mol. water which is given off at  $163^\circ$ , the melting point of the base, which at the same time acquires a yellow or brown colour. On further heating it quickly gives off gas and detonates. Nitropapaverine dissolves in 3,100 pts. ether at  $12^\circ$ ; sparingly in cold alcohol; with moderate facility in boiling alcohol; sparingly in boiling benzene; easily in chloroform; not at all in water, potash-ley, or ammonia. It is tasteless, and does not redden litmus; its salts have a bitter taste and acid reaction. Acetic acid dissolves the base with difficulty, and only when employed in large excess. Strong sulphuric acid dissolves it in the cold with yellow, at  $150^\circ$  with a dirty dark brown colour.

**Nitropapaverine hydrochloride**,  $C^{21}H^{28}(NO^2)NO^4.HCl + 1\frac{1}{2}H^2O$ , forms pale yellow, silky, delicate prisms; dissolves in 288 pts. water at  $16^\circ$ , freely in boiling water and alcohol; easily forms supersaturated solutions. With *mercuric chloride* it forms a yellowish amorphous double salt, insoluble in cold water, moderately soluble in hot water and hot alcohols. The *platinic-chloride*,  $2(C^{21}H^{28}(NO^2)NO^4.HCl).PtCl_4$ , is a yellow crystalline precipitate, soluble in water and in dilute acids. The *auro-chloride* is a yellow amorphous precipitate, very slightly soluble in boiling water.

The *hydrobromide* forms yellow prisms slightly soluble in water. The *hydriodide*,  $C^{21}H^{28}(NO^2)NO^4.HI$ , is precipitated by potassium iodide from a hot dilute solution of the hydrochloride, in rectangular laminæ or short prisms having the colour of lead iodide, very slightly soluble in hot water.

The *nitrate*,  $C^{21}H^{28}(NO^2)NO^4.NO^3H + H^2O$ , is obtained by adding sodium nitrate to the hot dilute solution of the hydrochloride, and recrystallising the precipitate from hot water. It likewise separates instantly on mixing the concentrated solution of the acetate with nitric acid, as a gelatinous precipitate, which is quickly converted into fine prisms. It is sparingly soluble in boiling water, and almost insoluble in cold water.

**PARAFFINS**,  $C^xH^{2x+2}$ . *Boiling points*.—The boiling points of the normal paraffins, that is of those whose carbon-atoms form a single chain, are as follows:—

	Boiling point	Difference
Butane, $C^4H^{10}$ . . . . .	$1^\circ$	
Pentane, $C^5H^{12}$ . . . . .	38	37°
Hexane, $C^6H^{14}$ . . . . .	70	32
Heptane, $C^7H^{16}$ . . . . .	99	29
Octane, $C^8H^{18}$ . . . . .	124	25
Dodecane, $C^{12}H^{26}$ . . . . .	202	4 x 10
Heedecane, $C^{18}H^{38}$ . . . . .	278	4 x 19

From this it appears that the boiling point is not raised  $31^\circ$  for each addition of  $CH^2$ , as formerly assumed, but that from the lower to the higher terms of the series the difference between the boiling points decreases by  $4^\circ$ , till it becomes the well-known difference of  $19^\circ$  (Schorlemmer, *Proc. Roy. Soc.* xvi. 367).

On the Refraction-equivalents of the Paraffins, see LIGHT (p. 740).

**Action of Chlorine**.—When chlorine is passed into a liquid paraffin, a portion of the monochloride first formed is always further acted on by the chlorine before all the hydrocarbon has been attacked; but the formation of such higher chlorides may be almost completely avoided by bringing the chlorine in contact with the vapour of the boiling hydrocarbon; the monochlorides, being less volatile than the higher chlorides, condense at once, and are thus brought out of the reach of an excess of chlorine.

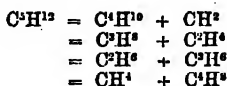
When any paraffin higher than ethane is thus treated with chlorine, two monochlorinated derivatives are obtained, a primary and a secondary; and these, when heated with potassium acetate and glacial acetic acid, are converted into the corresponding acetates. Neither the chlorides nor the acetates can be satisfactorily separated from one another by fractional distillation, but by heating the mixed acetates with potash, they are transformed into a primary and a secondary alcohol, the separation of which may be very completely effected by fractional distillation (Schorlemmer, *Phil.*

*Trans.* 1872, p. 111; *Ann. Ch. Pharm.* clxi. 263; *Chem. Soc. J.* x. 1038; xi. 319). See further, **HEXANE**, **HEPTANE**, and **OCTANE**, in this volume.

**Formation of Olefines from Paraffins.**—Any paraffin whatever, except marsh-gas, is theoretically resolvable into a paraffin of lower order, and one or more olefines, according to the general equation:



For example,



One example of this decomposition has long been known, viz. the resolution of butane  $C^4H^{10}$  into ethane  $C^2H^6$  and ethene  $C^2H^4$ , in the action of zinc on ethyl iodide, whereby butane is first formed according to the equation  $2C^2H^5I + Zn = ZnI^2 + C^4H^{10}$ , and then decomposed in the manner just mentioned (1st *Suppl.* 706); and it has lately been shown by Thorpe & Young (*Ann. Ch. Pharm.* clxv. 1; *Chem. Soc. J.* [2], ix. 342; x. 802) that solid paraffin, exposed to a high temperature in a closed vessel, is almost completely resolved, with evolution of but little gas, into liquid hydrocarbons. This conversion is readily effected on a small scale by sealing up a few grams of solid paraffin into a U-tube of hard glass surrounded by wire-gauze. The limb containing the paraffin is gently heated in a combustion-furnace, and as soon as it has distilled over, the gas is turned down, and the tube when cold is reversed, and the paraffin distilled again; on repeating this process, the paraffin becomes softer and softer, and at last remains liquid. When solid paraffin is heated under the common pressure in a vessel connected with inverted condensers, it is not altered, and further, it appears that only the higher members of the paraffin series undergo this decomposition. Thus a mixture of paraffins and olefines boiling at about  $225^\circ$  was not at all changed by treating it as above described.

To gain further insight into the nature of this decomposition,  $3\frac{1}{2}$  kilograms of paraffin from shale, melting at  $46^\circ$ , and composed of 85.14 p.c. carbon and 14.81 hydrogen, were heated in an apparatus consisting of two wrought-iron mercury bottles, connected by a bent iron tube provided with stopcock and valves. One of these bottles was charged with the paraffin and heated over an ordinary coal fire, the heat being so regulated as to produce a pressure of 20 to 25 pounds per square inch in the apparatus; the other bottle served as a condenser to receive the volatilised products. The operation was completed in four or five hours.

The liquefied product thus obtained amounted to 4 litres of liquid hydrocarbons, consisting of a mixture of paraffins and olefines. This mixture was fractionally distilled, the separate fractions were treated with bromine, and the bromides  $C^mH^{2m}Br^2$  were separated from the paraffins  $C^mH^{2m+2}$ . If the bromides decomposed during distillation, they were converted into the brominated derivatives  $C^mH^{2m}Br$  by boiling with alcoholic potash.

	Boiling point	Specific gravity
Pentane, $C^5H^{12}$ . . . . .	35–37°	
Hexane, $C^6H^{14}$ . . . . .	67–68	0.6631 at $18^\circ$
Heptane, $C^7H^{16}$ . . . . .	97–99	0.6913 „ $18.6$
Octane, $C^8H^{18}$ . . . . .	122–125	0.7165 „ $15.6$
Nonane, $C^9H^{20}$ . . . . .	147–148	0.7279 „ $13.6$

The brominated products obtained were:—

$C^5H^{12}Br^2$ . . . . .	184–188°	
$C^6H^{14}Br^2$ . . . . .	195–200	1.5967 at $20^\circ$
$C^7H^{16}Br^2$ . . . . .	Decomposed when heated	1.5146 „ $18.6$
$C^8H^{18}Br$ . . . . .	185–190	
$C^9H^{20}Br$ . . . . .	208–212	

The chloride,  $C^9H^{18}Cl^2$ , boils at about  $235^\circ$  with decomposition.

A paraffin of high boiling point obtained in the distillation of paraffin-oil from Bog-head coal is described by J. Galletly (*Chem. News*, xxiv. 227). It looks like bees-wax, but is crystalline and does not exhibit a conchoidal fracture. It melts at about  $80^\circ$ , boils at a red heat, and is partly resolved by distillation into liquid hydrocarbons.

The solubility of paraffin in benzene is less, and its specific gravity is greater, the higher its melting point, as may be seen from the following table:—



With *acetyl chloride*, sodium-nitromethane might be expected to yield nitro-acetone according to the equation :



but, on adding water after the violent reaction was over, white flakes separated out, probably consisting of a condensation-product (Meyer a. Rilliet).

Sodium-nitromethane, treated with *ethyl chlorocarbonate* in presence of absolute alcohol or ether, forms a brown oily body—not improbably ethyl nitroacetate—which is carbonised by distillation (Meyer a. Rilliet).

*Bromonitromethanes*.—The monobrominated compound,  $\text{CH}^3\text{Br.NO}^2$ , is formed by the action of bromine on dry sodium-nitromethane. It is a limpid, heavy, very refractive liquid, boiling at  $143^\circ$ – $144^\circ$ , very caustic, having a pungent irritating smell and acid reaction.

*Dibromonitromethane*,  $\text{CHBr}^2\text{NO}^2$ , is not easily formed. The best yield was obtained by cooling equivalent quantities of the monobromo-compound and aqueous potash with ice, mixing them rapidly, and pouring the solution into well-cooled bromine; some bromopictin is formed at the same time. Dibromonitromethane is a colourless liquid having a very irritating odour, and boiling with decomposition at  $155^\circ$ – $160^\circ$  (J. Tscherniak, *Deut. Chem. Ges. Ber.* vii. 916).

*Nitroethane*,  $\text{C}^2\text{H}^5\text{NO}^2 = \text{CH}^3\text{CH}^2\text{NO}^2$ , is formed by the action of silver nitrite on ethyl iodide, and is easily obtained pure by distillation and rectification in an oil-bath. Some nitrous ether is always formed at the same time, and about a fifth part of the ethyl iodide escapes decomposition, even when it is heated for a long time in a sealed tube with excess of silver nitrite.

Nitroethane is a colourless, strongly refractive liquid, having an agreeable and peculiar ethereal odour. Sp. gr. = 1.0582. Boiling point,  $111^\circ$ – $113^\circ$  (ethyl nitrite boils at  $16^\circ$ ). The vapour is inflammable and burns with a pale yellow flame, but does not detonate, even when heated considerably above its boiling point. By reduction with iron and acetic acid it is converted into amido-ethane (ethylamine),  $\text{C}^2\text{H}^5\text{NH}^2$  (Meyer a. Stüber, *Deut. Chem. Ges. Ber.* v. 399). With acetic anhydride it forms a crystalline solid melting at low temperatures, and apparently consisting of nitro-ethyl-methyl ketone,  $\text{C}^2\text{H}^5\text{NO}^2\text{CO.CH}^3$  (Meyer a. Wurster, *ibid.* 1029).

When nitroethane is dissolved in well-cooled fuming sulphuric acid, and the mixture is gently heated, a very violent reaction sets in, gases being evolved and ethene-disulphonic acid being formed.

A solution of nitroethane in common sulphuric acid undergoes on standing a violent decomposition if the quantity of acid is not large. But by using an excess (about 15 times) and working with small portions, a reaction sets in only when the liquid is boiled carefully for a few minutes. The products consist of acetic acid and a small quantity of another acid, forming an amorphous barium salt. The latter acid is produced in larger quantity by acting on nitroethane with well-cooled fuming acid for several days (Meyer a. Wurster, *ibid.* vi. 1168).

*Sodium-nitroethane*,  $\text{C}^2\text{H}^5\text{Na}(\text{NO}^2) = \text{CHNa}(\text{NO}^2)\text{CH}^3$ , is easily formed, either by heating a solution of nitroethane in anhydrous benzene with sodium, or by the addition of an alcoholic soda-solution to nitroethane. In the first case the sodium is converted, with violent evolution of gas, into a white powder which, after washing with ether, is the pure sodium-compound. In the second case the mixture becomes warm and at once solidifies to a white mass, which simply requires to be washed on the filter with absolute alcohol, and to be dried in the water-bath. The second method of preparation also affords a ready method of detecting nitroethane; owing to the slight solubility of the sodium-derivative in cold alcohol, even traces of nitroethane yield a precipitate on the addition of an alcoholic soda-solution. Neither alcoholic potash nor alcoholic ammonia produces a precipitate with nitroethane.

Sodium nitroethane is a white, apparently amorphous powder, which explodes only at temperatures above  $100^\circ$ ; it is extremely soluble in water, acids precipitating unchanged nitroethane from the solution. The aqueous solution is not precipitated on the addition of barium chloride or lead acetate; mercurous nitrate causes a grey, silver nitrate, a white precipitate, the latter rapidly becoming brown and finally black; copper sulphate produces a deep green, ferric chloride a blood-red solution. On the addition of mercuric chloride, the solution solidifies, after a short time, to a mass of crystalline needles which have the composition  $\text{HgClC}^2\text{H}^5\text{NO}^2$ , and may be regarded either as  $\text{Hg} \begin{Bmatrix} \text{Cl} \\ \text{C}^2\text{H}^5\text{NO}^2 \end{Bmatrix}$ , or as  $\text{Hg} \begin{Bmatrix} \text{C}^2\text{H}^5\text{NO}^2 \\ \text{C}^2\text{H}^5\text{NO}^2 \end{Bmatrix} + \text{HgCl}^2$  (Meyer a. Stüber, v. 514).

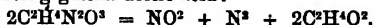
When an aqueous solution of sodium-nitroethane, or a solution of nitroethane in caustic potash or soda, is mixed with potassium nitrite and acidulated with sulphuric acid, no nitroethane is precipitated; but on agitating with ether, and leaving the

etheral solution to evaporate, splendid crystals are obtained, grouped in druses like prohnite. These crystals consist of ethyl-nitrolic acid,  $C^2H^3NO^3$ , or  $CH^3.CO.NH.NO^2$ , and their formation may be represented by the equation:



The same compound is obtained by dissolving nitroethane in alcoholic potash, adding sulphuric acid, agitating with ether, and evaporating. In this case, part of the nitroethane appears to give up  $NO^2$  to the potash, forming potassium nitrite, which then acts on the remaining nitroethane as above.

Ethyl-nitrolic acid melts at  $80^\circ-81^\circ$ , and quickly decomposes, giving off nitrogen and its tetroxide, and leaving glacial acetic acid:



The ethyl-nitrolates of potassium, sodium, ammonium, and bromine dissolve in water with deep red colour; those of the heavy metals are coloured very unstable precipitates, easily changing into nitrites. The lead salt has a brilliant orange colour, the silver salt is egg-yellow (V. Meyer, *Deut. Chem. Ges. Ber.* vii. 425).

Ethyl-nitrolic acid is the representative of a class of acids called nitrolic acids, having the general formula,  $C^xH^{2x}N^2O^3$ .

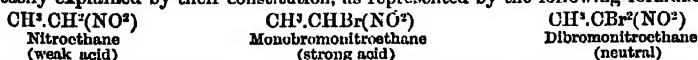
*Methyl-nitrolic acid*,  $CH^3N^2O^3$ , is obtained from nitromethane, by a reaction similar to the above, in small granular crystals (Meyer, *ibid.* vi. 1492).

*Bromonitroethanes* (Meyer a. Wurster, *ibid.* vi. 94; J. Tschorniak, *ibid.* vii. 916).—By adding bromine to sodium-nitroethane, a heavy oil is obtained, boiling at  $152^\circ-157^\circ$ , and consisting of a mixture of nitroethane with its mono- and dibrominated derivatives.

*Monobromonitroethane*,  $CH^3-CHBr(NO^2)$ , can be obtained nearly pure by a long-continued fractional distillation. It is a very heavy oil, smelling like chloropierin, and boiling at  $145^\circ-148^\circ$  (Meyer a. Wurster),  $155^\circ-160^\circ$  (Tschorniak). It dissolves in strong aqueous potash or ammonia, with evolution of heat, and yields crystalline compounds with a concentrated soda-solution and alcoholic ammonia. These salts, however, always contain some metallic bromide, and for this reason it is impossible to purify the crude monobromonitroethane by dissolving it in alkalis and precipitating it with acids, the product thus formed having a less constant boiling point than the original substance, and leaving on distillation a residue, which decomposes with deflagration and formation of a dense black smoke.

*Dibromonitroethane*,  $CH^3-CBr^2(NO^2)$ , has no acid properties, and can easily be obtained pure by treating the higher-boiling fraction with potash. It is a limpid, mobile liquid, having the same pungent smell as the monobromo-compound, and boiling at  $162^\circ-164^\circ$  (Meyer a. Wurster),  $155^\circ-160^\circ$  (Tschorniak).

The different degrees of acidity of nitroethane and its two brominated derivatives are easily explained by their constitution, as represented by the following formulæ—



Nitroethane and its monobromo-derivative contain hydrogen and nitril in association with the same carbon-atom, the hydrogen being therefore rendered replaceable by metals, in consequence of its proximity to the negative nitril; both are therefore acid, but in the second the acid character is enhanced by the introduction of another negative radicle, viz. the bromine. In dibromonitroethane, on the other hand, both the basylous hydrogen-atoms of nitroethane are replaced by bromine, and therefore the compound is neutral (Meyer a. Tschorniak, *Deut. Chem. Ges. Ber.* vii. 712).

**Nitropropanes**,  $C^3H^5NO^3$ . *Normal Nitropropane*,  $CH^3-CH^2-CH^2NO^2$ , is produced, together with propyl nitrite, by the action of propyl iodide on silver nitrite mixed with an equal volume of sand. It is a limpid mobile liquid very little heavier than water, and boiling at  $122^\circ-127^\circ$ . Its properties are similar to those of nitroethane. Its sodium salt gives characteristic precipitates with salts of the heavy metals (p. 896) (Meyer a. Rilliet, *Deut. Chem. Ges. Ber.* v. 1029). On dissolving it in aqueous potash, adding potassium nitrite and sulphuric acid, agitating with ether, and evaporating, propyl-nitrolic acid,  $C^3H^5N^2O^3$ , or probably  $CH^3.CH^2.CO.NO^2.NH$ , is obtained in long silky needles (Meyer a. Locher, *ibid.* vii. 670).

*Isonitropropane*,  $CH^3-CH(NO^2)-CH^3$ , is obtained, together with isopropyl nitrite, in a similar way as the other nitro-compounds. It boils at  $112^\circ-117^\circ$ . Its sodium-compound is deliquescent, and more soluble than that of normal nitropropane.

When potassium nitrite and sulphuric acid are added to an alkaline solution of isonitropropane, a deep blue liquid is obtained, which soon deposits a white sandy crystalline powder, isomeric with propyl-nitrolic acid, but not possessing acid properties.

It is called *propyl-pseudonitrol*, and has probably the constitution  $\text{CH}^3\text{C}(\text{NO})(\text{NO}^2)\text{CH}^3$ . It is insoluble in water, acids, and alkalis, almost insoluble in cold ether, more freely soluble in cold alcohol and chloroform, readily in the hot liquids. Its solutions have a pure blue colour, and it separates on evaporation in white glistening rhombohedrons resembling calcite. When heated it melts with partial decomposition, forming a deep blue liquid (Meyer a. Locher, *ibid.* vii. 670).

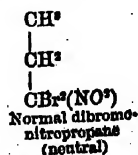
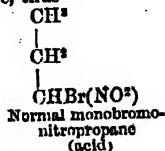
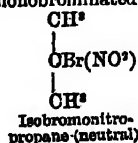
The heavy metals give, with the sodium-compounds of nitromethane, nitroethane, and the two nitropropanes, such characteristic precipitates that these reactions may be used for distinguishing these nitro-compounds, as the following table shows. Nitropentane does not form metallic compounds.

*Reactions of Nitroparaffins with Metallic Salts* (Meyer a. Chojanacki, *Deut. Chem. Ges. Ber.* v. 1034).

	Mercuric chloride	Mercurous nitrate	Ferric chloride
Sodium nitromethane	Light yellow precipitate; explosivo	Black flocculent precipitate	Dark brownish-red precipitate
Sodium nitroethane	White crystalline precipitate	Dirty-grey precipitate	Blood-red coloration
Sodium nitropropane (normal)	White crystalline precipitate	Black flocculent precipitate	Blood-red solution
Sodium nitropropane (iso)	White crystalline precipitate	Black flocculent precipitate	Blood-red solution

	Barium chloride	Copper sulphate	Lead acetate	Silver nitrate
Sodium nitromethane	0	Grass-green precipitate	White precipitate	White precipitate, turning almost immediately black
Sodium nitroethane	0	Deep green solution	0	White precipitate, soon turning brown
Sodium nitropropane (normal)	0	Deep green solution	White precipitate	White precipitate, gradually turning brown
Sodium nitropropane (iso)	0	Deep green solution	0	Light yellow precipitate, soon turning black

*Bromonitropropanes.*—Nitroethane, as already explained (p. 895), yields a monobromo-derivative which is more strongly acid than itself, and a dibromo-derivative which is neutral. If other nitro-paraffins behave in the same manner, those which contain a primary alcohol-radicle will also yield an acid monobrominated and a neutral dibrominated derivative, while those containing secondary radicles will yield only a neutral monobrominated derivative, thus—



The correctness of this view is shown by the following facts:—On gradually adding 1 mol. of bromine to a solution of 1 mol. of isonitropropane in 1 mol. of strong potash, pure monobromisonitropropane,  $\text{CH}^3\text{OBr}(\text{NO}^2)\text{CH}^3$ , separates out as a



heavy, strongly refracting oil, boiling, after one rectification, at  $148^{\circ}$ – $150^{\circ}$ , and having a pungent smell. It is perfectly insoluble in strong potash.

When normal nitropropane is treated in the same way, a mixture is obtained, from which the neutral dibromo-compound can easily be isolated by treating the highest-boiling fraction with strong potash. It is an oily liquid, having a pungent smell, and boiling at  $184^{\circ}$ – $186^{\circ}$ . It is quite insoluble in alkalis. The monobromo-compound can only be purified by continued fractional distillation; it is a similar liquid, boiling for the most part at  $155^{\circ}$ – $160^{\circ}$ . It dissolves in potash with evolution of heat, and is separated again by acids (Meyer a. Tscherniak, *Deut. Chem. Ges. Ber.* vii. 712; see further Tscherniak, *ibid.* 916).

**Nitro-isobutane**,  $C^4H^9(NO^2) = CH(CH^3)^2 - CH^2(NO^2)$ . This body was obtained, together with isobutyl nitrite, by acting with isobutyl iodide on a mixture of silver nitrite and sand. It is a pale-yellow light oil, smelling like peppermint, and boiling at  $137^{\circ}$ – $140^{\circ}$ . It is soluble in potash and reprecipitated by acids, but does not give a crystalline compound with alcoholic soda. By iron and acetic acid it is reduced to isobutylamine. It reacts energetically with sulphuric acid, forming isobutyric acid. On dissolving it in an equivalent quantity of potash, and adding bromine, a liquid separates which appears to consist of unaltered nitrobutane, monobromonitrobutane, and dibromonitrobutane. This latter is a pungent oil boiling at  $180^{\circ}$ – $185^{\circ}$  (E. Demoll, *ibid.* vii. 709, 790).

**Nitropentane**,  $C^5H^{11}NO^2$ , is formed by the action of silver nitrite on amyl iodide, the action being completed by the heat of an oil-bath. By fractional distillation of the product, portions were obtained boiling at  $148^{\circ}$ – $153^{\circ}$ ,  $152^{\circ}$ – $156^{\circ}$ , and  $156^{\circ}$ – $160^{\circ}$ , the greater part passing between  $150^{\circ}$  and  $160^{\circ}$  (ordinary amyl nitrite boils at  $95^{\circ}$ ). Nitropentane is strongly acted on by iron and acetic acid, the product giving off an ammoniacal odour on addition of potash. Heated with aqueous potash to  $100^{\circ}$  in sealed tubes, it gives a product from which sulphuric acid precipitates a heavy oil, not more than  $\frac{1}{3}$  of which distils between  $80^{\circ}$  and  $100^{\circ}$ , and a small quantity above  $160^{\circ}$  (Meyer a. Stüber, *ibid.* v. 203).

**PARALDEHYDE.** See ALDEHYDE (p. 33).

**PARA-OXYBENZOIC ACID.** This modification of the acid  $C^6H^4O^2$  is formed, together with oxybenzoic acid, by the action of melting potash on potassium sulphobenzoate. Slight variations in the mode of preparing the sulphobenzoic acid appear to influence the proportions of the two oxy-acids obtained from it; the largest amount of para-oxybenzoic acid was obtained from sulphobenzoic acid, prepared by exposing benzoic acid to the vapour of sulphuric anhydride, treating the agglomerated mass with fuming sulphuric acid, and gently warming for a short time.

The two oxy-acids cannot be separated by fractional crystallisation, but a partial separation may be effected by adding barium hydrate to the solution of the barium salts of the two acids, whereby basic barium para-oxybenzoate is precipitated without any oxybenzoate, part of the basic para-salt, however, remaining dissolved (Ira Remson, *Zeitschr. f. Chem.* [2]. vii. 81).

Para-oxybenzoic acid is also formed, together with anol or allyl-phenol (1st Suppl. 175), by fusing anethol with potash (Ladenburg, *Ann. Ch. Pharm., Suppl.* viii. 87).

**PARASORNIC ACID.** See SORNIC ACID.

**PARATHIONIC ACID.** This name was given by Gerhardt to a supposed isomerido of ethyl-sulphuric acid, the barium salt of which was said to be obtained by boiling the solution of the ethyl sulphate (iv. 354). It has been shown, however, by Kelenmeyer (*Ann. Ch. Pharm.* clxii. 373) and by Scheibler (*Deut. Chem. Ges. Ber.* v. 446), that this supposed isomerido has no existence, the two barium salts being perfectly identical.

**PARISIN.** This alkaloid, obtained from a cinchona bark, has been shown by Flückiger to be identical with beberine (1st Suppl. 255).

**PARVOLINE**,  $C^8H^{11}N$ . This alkaloid has been shown by Vohl a. Eulenberg to be one of the constituents of tobacco-smoke (see TOBACCO).

**PATTINE**,  $C^{11}H^{21}NO + H^2O$ . An alkaloid obtained from a white cinchona bark from Payta in Peru (see CINCHONA-BASES, p. 347).

**PELARGONIC, or NONYLIC ACIDS**,  $C^9H^{19}O^2 = C^8H^{17}.COOH$ . 1. Pelargonic acid, prepared by the oxidising action of chromic acid mixture on methyl-nonyl ketone,  $C^{10}H^{20}O$ , from rue-oil (p. 808), and purified by conversion into sodium salt, separation by sulphuric acid, and rectification, forms a light oil which boils at  $248^{\circ}$ – $250^{\circ}$ , solidifies completely at  $0^{\circ}$ , and melts again at  $+7^{\circ}$ . Its barium and calcium salts, prepared

2nd Sup.

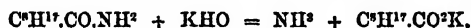
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by precipitating the ammonium salt with the corresponding chlorides, and purified by recrystallisation from hot water, form colourless leaflets unctuous to the touch. The *barium salt* is anhydrous. The *copper salt* is a light green precipitate insoluble even in boiling water, caking together to a resinous mass when heated in the liquid from which it is precipitated, melting in the dry state at  $258^{\circ}$ ; it dissolves in alcohol with deep green colour. The *silver salt* is a white precipitate nearly insoluble in boiling water (Giesecke, *Zeitschr. f. Chem.* [2], vi. 429).

2. The normal acid,  $\text{CH}_2^{\text{C}^{\text{H}^{\text{I}}}}(\text{CH}_2)^n\text{COOH}$ , called especially *nonylic acid*, is prepared from the normal octyl alcohol,  $\text{CH}_2^{\text{C}^{\text{H}^{\text{I}}}}(\text{CH}_2)^n\text{CH}_2\text{OH}$ , of Heracleum-oil, by converting this alcohol into octyl iodide, the latter into cyanide, heating the cyanide with alcoholic potash, and distilling the resulting potassium salt with sulphuric acid. The acid thus obtained is a colourless oily liquid having a faint odour, solidifying to a crystalline mass at low temperatures, and beginning to melt at  $+10^{\circ}$ ; the acid separated from the recrystallised silver salt melts at  $12^{\circ}$ – $12.5^{\circ}$ , solidifies at  $11.5^{\circ}$ , and gives the same results after distillation, solidification, and strong pressure. It boils at  $253^{\circ}$ – $254^{\circ}$  under a pressure of 758.8 mm., and has a specific gravity of 0.9065 at  $17.5^{\circ}$ . It dissolves sparingly in water and distils slowly with aqueous vapour.

The *potassium, sodium, and ammonium salts* form small pearly scales; the first is decomposed by hot alcohol, the third on warming its aqueous solution. The *barium, calcium, copper, zinc, and lead salts* separate in crystals from their aqueous solutions; the lead salt appears to be basic. The *methyl ether*,  $\text{C}^{\text{H}^{\text{I}}}(\text{CH}_2)^n\text{O}^{\text{I}}$ , is a colourless liquid of sp. gr. 0.8765 at  $17.5^{\circ}$  and boiling at  $213^{\circ}$ – $214^{\circ}$ . The *ethyl ether*,  $\text{C}^{\text{H}^{\text{I}}}(\text{C}^{\text{H}})_2\text{O}^{\text{I}}$ , has a specific gravity of 0.8655 at  $17.5^{\circ}$ , and boils at  $227^{\circ}$ – $228^{\circ}$  (Franchimont a. Zincke, *Deut. Chem. Ges. Ber.* v. 19).

3. *Isononylic acid*,  $\text{CH}_2^{\text{C}^{\text{H}^{\text{I}}}}\text{CH}^{\text{C}^{\text{H}^{\text{I}}}}\text{COOH}$  (Kuhlthom, *Ann. Ch. Pharm.* cxxxii. 319). This modification is obtained from methyl-hexyl carbinol (castor-oil alcohol) by converting the alcohol into the corresponding cyanide,  $\text{C}^{\text{H}^{\text{I}}}\text{CN}$  (isononyl nitril), and digesting this compound with alcoholic potash, whereby it is first converted, by assumption of  $\text{H}_2\text{O}$ , into isononylamide,  $\text{C}^{\text{H}^{\text{I}}}\text{CO.NH}_2$ , and afterwards into potassium isononylate:



which, when distilled with sulphuric acid, yields isononylic acid.

This acid is a colourless oil, almost insoluble in water, easily soluble in alcohol and ether. Sp. gr. = 0.90325 at  $18^{\circ}$ . Boils at  $244^{\circ}$ – $246^{\circ}$ . The *sodium salt* is a crystalline mass easily soluble in water and in alcohol; the *potassium salt* forms an amorphous soap. Both these salts may be salted out of their aqueous solution by addition of common salt. The *ammonium salt* is an oil insoluble in water, but soluble in alcohol. The *calcium salt*,  $\text{Ca}(\text{C}^{\text{H}^{\text{I}}}\text{O}^{\text{I}})_2 + \text{H}_2\text{O}$ , separates from hot water in masses of needles. The *copper salt* is a green precipitate, or a doughy mass which slowly becomes crystalline. The *silver salt* is a white precipitate which decomposes when heated to  $100^{\circ}$  or boiled with water. The *ethyl ether* is a colourless oil boiling at  $213^{\circ}$ – $215^{\circ}$  and having a specific gravity of 0.86406 at  $17^{\circ}$ .

*Isononylamide*,  $\text{C}^{\text{H}^{\text{I}}}\text{CONH}_2$ , forms small needles or scales which volatilise with water-vapour, melt at  $80^{\circ}$ – $81^{\circ}$ , and dissolve sparingly in cold water, readily in alcohol and ether. Its aqueous solution heated with mercuric oxide and allowed to cool, deposits mercuric isonylamide in tufts of needles melting at  $117^{\circ}$ – $118^{\circ}$  (Kuhlthom).

Pelargonic acid from oil of rue agrees in boiling point with isononylic acid much more nearly than with Franchimont a. Zincke's *nonylic acid*, from which it also differs considerably in its melting and solidifying points, and in the boiling point of its ethylic ether. It is therefore most probably identical with isononylic acid, whence it must be inferred that oil of rue contains isononylic aldehyde,  $\text{CH}_2^{\text{C}^{\text{H}^{\text{I}}}}\text{CH}^{\text{C}^{\text{H}^{\text{I}}}}\text{CHO}$ .

**PENTACHLORETHANE**,  $\text{C}^{\text{H}}\text{Cl}_5$ . This compound treated with alcoholic potash yields potassium chloride, and a potassium salt which crystallises in needles and probably has the composition  $\text{C}^{\text{H}}\text{Cl}_5\text{COK}$  (Hoch a. Kolbe, *J. pr. Chem.* [2], iv. 60).

On the action of bromine on pentachlorethane, whereby the compound  $\text{C}^{\text{H}}\text{Cl}_4\text{Br}$  is produced, see CARBON CHLORIDES (p. 258).

**PENTACHLOROMETHYL OXIDE**,  $\text{C}^{\text{H}}\text{Cl}_5\text{O}$ . See ETHYL OXIDE (p. 484).

**PENTANE**,  $\text{C}^{\text{H}}_5$ . See AMYL HYDRIDE (p. 63).

**PERCHLOROMETHYL-MERCAPTAN**,  $\text{CCl}_5\text{S}$ . See CARBON SULPHO-CHLORIDES (p. 266).

**PERCYLITE**,  $\text{Pb}^2\text{Cl}^2\text{O} \cdot \text{Cu}^2\text{Cl}^2\text{O} \cdot \text{H}^2\text{O}$ . This mineral, originally found at Sonora in Mexico, where it occurs crystallised in cubes (iv. 377), has also been found in South Africa, sometimes in very minute but confused crystals, but generally massive, or as a coating, or in veins, associated with anglesite, cerussite, and chlorargyrite. In this, as well as in the Mexican specimens, the blue colour changes to emerald-green on heating, and reappears on cooling (Maskelyne & Flight, *Chem. Soc. J.* [2], x. 1051).

**PERIDOTE**. Crystals of this mineral are formed, together with crystals of pyroxene, by heating its constituents, silica, alumina, and magnesia, with calcium chloride (Lechartier, *Compt. rend.* lxxv. 487; *Chem. Soc. J.* [2], xi. 40).

**PERIODIDES**. See IODINES (p. 677).

**PERSOWSITE**,  $\text{CaO} \cdot \text{TiO}^2$ . This mineral, though belonging to the regular system, has been found by Hesseberg (*Jahrb. f. Mineralogie*, 1871, 640) to be doubly refractive and optically uniaxial. As, however, a revision of the angular measurements left no doubt of the monometric character of the crystals, and as this result has been confirmed by G. vom Rath (*Pogg. Ann.* cxliv. 595), the double refraction must be attributed to an internal transformation of the substance.

**PEROXIDES**. *Preparation by Electrolysis*.—W. Wernicke (*Pogg. Ann.* cxli. 109) has prepared several peroxides by subjecting metallic solutions to the action of a two-cell Daniell's battery, the positive electrode being a plate of platinum, and the negative consisting of two sheets of platinum, placed one on each side of the positive electrode.

*Lead*.—An alkaline solution of lead and sodium tartrate gave a brilliant, bluish-black deposit of  $\text{PbO}^2 \cdot \text{H}^2\text{O}$ , sp. gr. 6.267. A solution of 1 pt. lead nitrate in 8 pts. water gave, by 36 hours' treatment, anhydrous  $\text{PbO}^2$ , sp. gr. 9.045. By treatment for a shorter time, or by using more dilute solutions, products are obtained containing variable quantities of water. It appears that the acid set free at the positive electrode abstracts water from the peroxide, for anhydrous lead peroxide placed in connection with the positive electrode in water containing a little soda, passed into  $\text{PbO}^2 \cdot \text{H}^2\text{O}$ . The quantity of oxygen in the oxide varies inversely as the strength of the current, for by using six elements of Bunsen's battery, pure hydrated lead oxide was formed.

*Manganese*.—The preparation of manganese peroxide requires a weaker current. The acetate and nitrate gave  $\text{MnO}^2 \cdot \text{H}^2\text{O}$ , sp. gr. 2.564.

*Bismuth*.—Two elements of Daniell's battery gave, with a solution of basic bismuth nitrate in sodium tartrate, a black deposit of  $\text{BiO}^2 \cdot \text{H}^2\text{O}$ , sp. gr. 5.571.

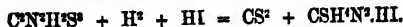
*Cobalt*.—An aqueous solution of cream of tartar and hydrated cobalt oxide with a little soda gave  $\text{CoO}^2 \cdot 2\text{H}^2\text{O}$ , sp. gr. 2.483.

*Nickel*.—A solution of nickel analogous to that last mentioned gave  $\text{NiO}^2 \cdot 2\text{H}^2\text{O}$ , sp. gr. 2.744.

**PERSEA**. The rind, kernel, and fresh pulp of the Avocado pear (*Persea gratissima*), which is eaten in Mexico as a cream with lime-juice, wine, and sugar, have been analysed by L. Glutz (*Arch. Pharm.* [2], cxlvi. 114; *Chem. Soc. J.* [2], ix. 727); 100 pts. of the dried pulp contain 5.109 pts. of ash and 1.353 nitrogen.

**PERSULPHIDE OF HYDROGEN**,  $\text{H}^2\text{S}^2$ . See SULPHIDES.

**PERSULPHOCYANIC ACID**,  $\text{C}^2\text{N}^2\text{H}^2\text{S}^2$  (iv. 378). This compound, treated in aqueous solution with phosphorus iodide (i.e. with nascent hydriodic acid), yields— together with carbon sulphide and hydrogen sulphide—the hydriodide of sulphurea, which crystallises from hot water in waxy tabular plates:



The hydrogen sulphide is doubtless a product of the action of the hydrogen iodide on the carbon sulphide.

Persulphocyanic acid, treated with tin and hydrochloric acid, dissolves, with evolution of hydrogen sulphide and carbon sulphide, and forms the stannochloride of sulphurea.

*Aniline*, with the aid of heat, dissolves about half its weight of persulphocyanic acid, and solidifies to a grey mass, which crystallises from boiling alcohol in nacreous scales having the composition  $\text{C}^2\text{H}^2\text{S}^2\text{N}^2$ :



This compound—which may be regarded as a biuret having its oxygen replaced by sulphur, and 1H by  $\text{C}^2\text{H}^2$ —is insoluble in water, whether hot or cold, and possesses both acid and basic properties. From solution in soda or ammonia it is precipitated by hydrochloric acid. Its hydrochloride, obtained by dissolving it in dilute aqueous

ferric chloride, dissolves easily in warm water, and crystallises in needles. With *platinic chloride* it forms a double salt which crystallises in needles; with *stannic chloride* and *mercuric chloride* white precipitates. The *oxalate*, *nitrate*, and *sulphocyanate* are sparingly soluble; the *sulphate* is easily soluble (L. Glutz, *Ann. Ch. Pharm.* cliv. 39, 44, 48).

According to A. Fleischer (*Deut. Chem. Ges. Ber.* iv. 100), an alcoholic solution of persulphocyanic acid forms with silver nitrate a yellow precipitate, with mercuric chloride a white precipitate. On boiling it with mercuric oxide, the solution on cooling deposits a beautifully crystallised mercury salt. With iodine very fine crystals are obtained, having a peculiar golden-yellow lustre.

**PERTHIOSULPHANHYDRIDE.** See PERSULPHIDE OF HYDROGEN, under SULPHIDES.

**PETALITE.** The crystals of petalite from Elba have been described by G. vom Rath and G. Strüver (*Jahrb. f. Mineralogie*, 1870, 690). The axial ratio  $a : b : c = 1.15342 : 1 : 0.743686$ ; angle  $ac = 122^\circ 26'$ ; whence  $\infty P : \infty P = 86^\circ 20'$ .

**PETROLEUM.** On the Physical Properties and Heating Power of different Petroleum from Russia, see H. Sainte-Claire Deville (*Compt. rend.* lxxii. 191; *Chem. Soc. J.* [2], ix. 453).

On the Hydrocarbons from the Petroleum of Pechelbronn, see J. Le Bel (*Compt. rend.* lxxiii. 499, lxxv. 267; *Chem. Soc. J.* [2], ix. 1025, x. 886).

On the Hydrocarbons of Pennsylvanian Petroleum: H. Byasson (*Compt. rend.* lxxiii. 609; *Chem. Soc. J.* [2], ix. 1024).

On the Influence of Sunlight on Petroleum Oils: Grabowski (*Pharm. J. Trans.* [3], ii. 226; *Chem. Soc. J.* [2], ix. 1025).

On the Determination of the Igniting Points of Petroleum Oils: B. H. Paul (*Chem. News*, xxi. 2); F. C. Calvert (*ibid.* 85); List (*Wagner's Jahresbericht*, 1870, 708); Van der Weyde (*Zeitschr. anal. Chem.* xi. 338; *Chem. Soc. J.* [2], xi. 532).

On Petroleum Exploration in Galicia and America, see A. Fauck (*Dingl. pol. J. cervi.* 158).

**PHENACITE.** *Glucinum silicate* (iv. 387).—This mineral quickly loses its colour by keeping. A dark wine-yellow crystal was observed by Kokscharow (*Jahrb. f. Mineralogie*, 1870, 103) to become perfectly colourless in two months.

**PHENACONIC ACID.** This name was given by Carius to an acid isomeric with acetic acid, obtained by the action of baryta-water on trichlorophenomalic acid (1st *Suppl.* 904). Subsequent researches have shown that it is identical with fumaric acid,  $C^4H^2O^4$  (*Deut. Chem. Ges. Ber.* iv. 928; *Chem. Soc. J.* [2], x. 144).

**PHENANTHRENE.** A hydrocarbon isomeric with anthracene (p. 84).

**PHENOL.**  $C^6H^5O = C^6H^4.OH$ . *Phenyl alcohol*.—1. A small quantity of this compound is formed, together with glycerin-ether and other products, when glycerin is distilled with calcium chloride (Linnemann a. v. Zotta, *Ann. Ch. Pharm., Suppl.* viii. 254); 14.8 kilograms of glycerin thus treated yielding 250 grains of glycerin-ether,  $(C^6H^5)^2O^2$ , and 18 grains of pure phenol (v. Zotta, *ibid.* clxxiv. 87). It appears, also, to be produced when glycerin is heated with zinc chloride or hydrogen-potassium sulphate, and by the action of a concentrated solution of potassium hydrate on glycerin-ether.

2. Dumas and Bardsy (*Compt. rend.* lxxiv. 1052) assert that monochlorobenzene,  $C^6H^5Cl$ , is converted by heating with aqueous sodium hydrate at  $300^\circ$  into phenol.

3. According to Lieben (*Ann. Ch. Pharm., Suppl.* vii. 240), the first fraction of the distillate from horse's urine contains phenol. It may be separated from the iodoform-yielding substance always furnished by urine, by distillation with a little potassium hydrate, and obtained from the residue by distilling with sulphuric acid. Hoppe-Seyler (*Chem. Soc. J.* [2], x. 628, from *Pflüger's Archiv. f. Physiologie*, v. 470) confirms this statement, and also the earlier observations of Stædeler and Buligin, that phenol can be obtained from urine by distilling it with sulphuric acid; he contends, however, that phenol is not originally contained in urine, but is formed by the action of the sulphuric acid, probably from indican. Similarly, Landolt's observation that bromine-water precipitates directly from urine tribromophenol, or at any rate a substance which yields phenol when treated with sodium-amalgam, does not prove the pre-existence of phenol, because other substances, such as the oxybenzoic acids, yield with bromine-water either tribromophenol or bodies which, on reduction, furnish phenol.

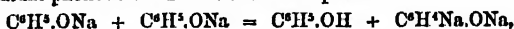
**Reactions.**—1. Landolt recommends bromine-water as the most delicate test for small quantities of phenol (*Deut. Chem. Ges. Ber.* iv. 770). When added in excess to dilute neutral or faintly acid solution of phenol, this reagent produces an immediate

bulky yellowish precipitate of tribromophenol. In order to ascertain whether the precipitate is tribromophenol, it is filtered off, and after washing is warmed gently in a test-tube with sodium-amalgam and water; the liquid is then poured into a small dish and acidulated, when, if phenol be present, the characteristic odour is at once perceived, and oily drops are seen floating in the liquid. By this reaction 1 part of phenol in 43,700 of water may easily be detected. Para-oxybenzoic acid, however, also yields tribromophenol, and salicylic acid is converted into dibromosalicylic acid, which furnishes phenol with sodium-amalgam and water; other members of the phenol group also furnish similar precipitates with bromine-water.

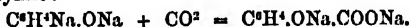
2. Phenol solutions, boiled with a solution of *mercurous nitrate*, assume a deep red colour, the production of which is due to the presence of a trace of nitrous acid; much more than a trace of this acid renders the colour indistinct. The reaction is very distinct with  $\frac{1}{60,000}$ th of phenol, and is still apparent when only  $\frac{1}{200,000}$ th is present. Salicyl and salicylic acid behave like phenol (Plugge, *Zeitschr. anal. Chem.* xi. 173).

3. A solution of phenol when mixed with one-fourth its volume of ammonia and a few drops of bleaching-powder solution (1 to 20 of water), and then warmed but not boiled, assumes a blue colour (green in very dilute liquids), becoming red on addition of sulphuric or hydrochloric acid. Solutions containing  $\frac{1}{4,000}$ th of phenol give a strong blue reaction (Salkowski, *Zeitschr. anal. Chem.* xi. 316).

4. The behaviour of sodium- and potassium-phenol with *carbonic anhydride* has been studied by Kolbe (*J. pr. Chem.* [2], x. 89). The action of carbonic anhydride on dry sodium phenol commences at a temperature below 100°, but is most rapid and complete at about 170°–180°; on raising the temperature gradually to 220°–250°, phenol distils over equivalent in amount to one-half the sodium-phenol. The operation is ended when phenol ceases to come over; the residue then consists entirely of disodium salicylate. The reaction appears to consist in the formation of 1 mol. of phenol and 1 mol. of disodium-phenol from 2 mol. of sodium-phenol:



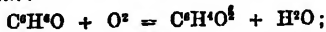
the latter of which combines, at the moment of formation, with carbonic anhydride to form disodium salicylate:



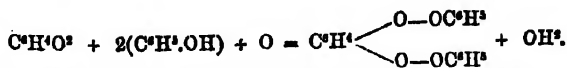
When potassium-phenol is similarly treated, the product varies according to the temperature at which the action takes place. At a temperature not exceeding about 145° salicylate only appears to be formed, but if the action take place at 170°–210°, about half the phenol employed as potassium-phenol distils over; scarcely any salicylate is formed however, but the product consists almost entirely of the isomeric para-oxybenzoate.

5. When phenol is fused with an excess of *potassium hydrate* until the mass assumes the consistence of a thick syrup, abundance of hydrogen is evolved, and a mixed product is obtained, containing, together with unattacked phenol, salicylic acid, oxybenzoic acid, diphenol, and other substances of unknown composition (Barth, *Ann. Ch. Pharm.* clvi. 93). At least half the phenol employed remains unaltered; the amount of acids produced does not exceed 1 p.c. of the phenol decomposed; 12 to 15 p.c. of the phenol employed is obtained in the form of diphenol.

6. When oxidised by *chromic acid* phenol is converted into phenoquinone,  $C^6H^4O^4$  (Wichelhaus, *Deut. Chem. Ges. Ber.* v. 248, 846). The first action appears to consist in the production of quinone:



the phenoquinone being formed from this compound and phenol in the following manner:



Phenoquinone is produced, together with hydroquinone and quinhydrone, when quinone is added to a solution of phenol:

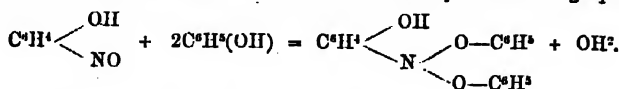


7. By the action of *nitrous acid* phenol is converted into nitrosophenol,  $C^6H^4NO.OH$  (Bayer, *Deut. Chem. Ges. Ber.* vii. 967).

8. When a solution of 6 p.c. of *potassium nitrite* in concentrated sulphuric acid is added to a mixture of equal volumes of phenol and concentrated sulphuric acid, the solution at first becomes brown, then green, and finally assumes a magnificent blue colour. The colouring matter is deposited in reddish-brown flocculi on pouring the

solution into water; it has the composition  $C^6H^3NO^3 = 3C^6H^4O + HNO^2 - 2OH^1$  (Liebemann, *ibid.* vii. 248, 1098).

The same compound is produced when nitrosophenol and phenol are mixed and concentrated sulphuric acid is added, and there can be little doubt that the first action of the nitrite mixture is to form nitrosophenol, which then enters into reaction with the unattacked phenol, perhaps in the manner indicated by the following equation:



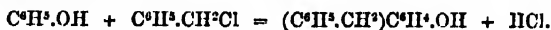
9. On distilling a mixture of phenol and *lead oxide*, a small portion undergoes conversion into diphenylene oxide,  $(C^6H^4)_2O$ . At the same time a small quantity of a second body crystallising in needles (m. p.  $173^\circ-174^\circ$ ) is obtained, which probably has the composition  $C^{12}H^6O^2$  (Graebe, *ibid.* vii. 396; Bohr a. van Dorp, *ibid.* 398).

10. The crystals obtained, together with phenyl sulphhydrate and sulphide, on distilling phenol with *phosphorus pentasulphide* (Kekulé a. Saueh) are identical with the phenylene sulphide obtained by Stenhouse. The compound, however, is a diphenylene disulphide,  $(C^6H^4)_2S_2$ , and not phenylene sulphide,  $C^6H^4S$  (Graebe, *ibid.* vii. 51, 397).

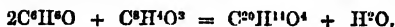
11. On adding phenol to *diazobenzene sulphate*, phenyl ether or oxide is produced (Hofmeister, *Ann. Ch. Pharm.* clix. 191):



12. When a mixture of *benzyl chloride* and phenol is gently heated with metallic zinc, hydrochloric acid is evolved in abundance and benzyl-phenol is produced (Paternò, *Gazzetta chimica italiana*, ii. 1):



13. When heated with phthalic anhydride and concentrated sulphuric acid, phenol is converted into phenol-phthalein (Bayer, *Deut. Chem. Ges. Ber.* iv. 658)—

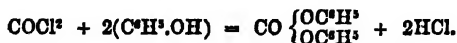
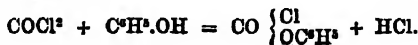


14. *Chromic chloride* (chlorochromic anhydride),  $C^6O^2Cl^2$ , acts violently upon phenol dissolved in glacial acetic acid, producing chiefly tri- and tetra-chloroquinone (Carstanjen, *J. pr. Chem.* [2], ii. 82).

15. *Nitrosyl chloride*,  $NOCl$ , acts readily upon phenol. According to Tilden (*Chem. Soc. J.* [2], xii. 851), it appears to oxidise the phenol to quinone, which is then converted into chlorinated quinones, the nitrosyl chloride itself suffering reduction, not merely to nitric oxide or nitrogen, but being converted in great part into ammonium chloride.

16. *Pyrosulphuric chloride*,  $S^2O^3Cl^2$ , at once attacks phenol and forms a mixture of the two isomeric monochlorophenols obtained on chlorinating phenol, with the corresponding chlorophenolsulphonic acids, sulphurous anhydride and hydrochloric acid being evolved (Armstrong and Pike, *Chem. News*, xxix. 283).

17. By heating phenol with carbonic chloride (phosgene) in sealed tubes at  $140^\circ-150^\circ$ , a mixture of phenyl chlorocarbonate and phenyl carbonate is obtained (Kempf, *J. pr. Chem.* [2], i. 402):



18. According to Dusart a. Bardy (*Compt. rend.* lxxiii. 1379) phenol is converted into monochlorobenzene,  $C^6H^4Cl$ , by the action of fuming *hydrochloric acid* at  $200^\circ$ . They also assert that mixtures of phenol and *methylic, ethylic, or amyl alcohol*, saturated with hydrochloric acid, furnish the corresponding mixed ethers when heated in sealed tubes at  $100^\circ$ . These statements, however, appear to require confirmation.

19. On heating phenol with *benzamide*, ammonia and benzoyl-phenol or phenylic benzoate,  $C^6H^4.O.CO^2C^6H^5$ , are produced; similarly phenol and acetamide yield acetyl-phenol or phenylic acetate,  $C^6H^4.O.COCH^3$ , and ammonia (Guarreschi, *Ann. Ch. Pharm.* clxxi. 140).

20. A dry mixture of potassium-phenol and *potassium benzoate* yields diphenyl on distillation,  $C^6H^4.OK + C^6H^4.CO^2K = (C^6H^4)_2 + K^2CO^3$ . An excess of benzoate is desirable, but the amount employed should not be more than double that required by theory. Similarly a mixture of *potassium acetate* and potassium-phenol furnishes

toluene,  $C^6H^5.OH^2$ , and a mixture of *potassium valerate* and potassium-phenol yields isobutylbenzene,  $C^6H^5.C^4H^9$ . A mixture of potassium-phenol and *potassium metanitrobenzoate* with sand gave nitrodiphenyl,  $C^6H^4.NO^2.C^6H^5$ , when carefully distilled. *Potassium oxalate* and potassium-phenol also furnish diphenyl. A mixture of *potassium acetate* and potassium-tribromophenol is said to yield tribromotoluene,  $C^6H^2.Br^3.CH^3$  (Pfankuch, *J. pr. Chem.* [2], vi. 97).

21. When *acetanilide* is distilled with sodium-phenol, diphenyl, aniline, acetone, and a very small quantity of a body having the properties of diphenylamine are produced. A trace of the latter body is also obtained on heating *sulphocarbonilide* with sodium phenol (Weith, *Deut. Chem. Ges. Ber.* vi. 966).

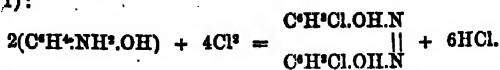
22. Berthelot (*Compt. rend.* lxxiii. 663) has determined the heat evolved on neutralising aqueous solutions of phenol and trinitrophenol by the alkaline hydrates. He finds that the heat furnished by the reaction of phenol with the hydrates of potassium, sodium, barium, and calcium is very nearly the same, and that it is scarcely influenced by the amount of water present (see HEAT, p. 620).

**Amidophenols.** *Para-amidophenol*,  $C^6H^4.NH^2.OH$  (1 : 4), first obtained by Fritzsche (*Ann. Ch. Pharm.* cx. 166), by the action of iron and acetic acid on paranitrophenol, is best prepared by reducing paranitrophenol with tin and hydrochloric acid; the excess of acid is removed by evaporating the solution, and after the addition of much water, the tin is precipitated by sulphuretted hydrogen; the solution is concentrated in a current of sulphuretted hydrogen, and then left to crystallise, when para-amidophenol hydrochloride separates in colourless plates (Schmitt a. Cook, *Kekulé Org. Chem.* iii. 61). Alkaline carbonates precipitate para-amidophenol from a solution of the hydrochloride as a brown-red crystalline powder soluble at 0° in 90 pts. of water and 22 pts. absolute alcohol. Para-amidophenol is also obtained on distilling amidosalicylic acid (Schmitt, *Deut. Chem. Ges. Ber.* i. 67). The *hydrochloride* dissolves at 0° in 1.4 pts. of water and 10 pts. of absolute alcohol; the *sulphate* crystallises in thin needles; the *acetate* melts at 183° and dissolves at 0° in 9 pts. of water and 12 pts. alcohol. By the action of benzoyl chloride at 150°, para-amidophenol hydrochloride is converted into benzoyl-para-amidophenol, which melts at 139° with partial decomposition. It is insoluble in water, and but slightly soluble in alcohol; boiling alcohol decomposes it (Morse, *ibid.* vii. 1319).

*Orthoamidophenol*,  $C^6H^4.NH^2.OH$  (1 : 2), is similarly prepared from orthonitrophenol (Schmitt a. Cook). It separates from the hydrochloride in white glistening rhombic plates (Körner), soluble at 0° in 59 pts. water and 23 pts. alcohol. *Orthoamidophenol hydrochloride* crystallises in long needles which dissolve at 0° in 1.25 pt. water and 2.36 pts. alcohol; the *sulphate* forms rhombic prisms; the *acetate* melts at 150°, and dissolves at 0° in 65 pts. water and 40 pts. alcohol. When heated with benzoyl chloride at 150°, orthoamidophenol hydrochloride furnishes benzoyl-orthoamidophenol,  $C^6H^3.OH.NH.COC^6H^5$ , which crystallises from alcohol in beautiful plates or prisms possessing an extremely pleasant odour. It melts at 103°; it is slowly decomposed by boiling water, in which it is soluble. Fuming nitric acid converts it into dinitrobenzoyl-orthoamidophenol, which forms thin straw-yellow needles melting at 173° (Morse).

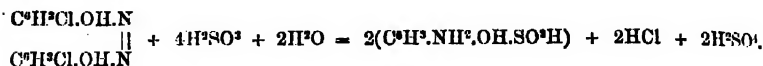
Para- and orthoamidophenol hydrochlorides are dissolved by Nordhausen sulphuric acid, with formation of the corresponding amidophenolsulphonic acids (Brackebusch, *ibid.* vi. 396).

*Dichlorazophenol*.—By the action of potassium permanganate solution and other oxidising agents, the amidophenols are converted into brown humus-like substances, orthoamidophenol being by far the more readily attacked; on treatment, however, of para-amidophenol hydrochloride with bleaching-powder solution, dichlorazophenol is produced, the reaction taking place with such precision that it may be employed for the quantitative analysis of bleaching-powder (Schmitt a. Bennewitz, *J. pr. Chem.* [2], viii. 1):



Orthoamidophenol does not yield a corresponding compound, but is acted upon in a manner not yet understood. To prepare dichlorazophenol, at most 3 grams of para-amidophenol hydrochloride are dissolved in 150 grams of water, and a rather concentrated solution of bleaching-powder is added from a burette. At first, white crystalline flakes separate, which redissolve on shaking, and the solution assumes a deep violet colour; on further addition of the bleaching-powder, a point is reached where the separated dichlorazophenol no longer redissolves, but the liquid becomes paler and suddenly turns yellow. The reaction is then completed. The product is separated by filtration, and after washing with water, dried over sulphuric acid. Dichlorazophenol

is sparingly soluble in cold water, but freely in boiling water, alcohol, benzene, ether, and glacial acetic acid; it crystallises in tufts of long yellow needles. It melts at  $86^{\circ}$ , and decomposes at a slightly higher temperature; it is extremely volatile, and has a very persistent odour like that of quinone. When reduced by tin or zinc and hydrochloric acid, it furnishes para-amidophenol. On treatment with sulphurous acid or hydrogen-sodium sulphite, it is entirely converted into para-amidophenolsulphonic acid:



**Paradiazophenol hydrochloride**,  $\text{C}^6\text{H}^4\text{N}^2\text{Cl}$ .—If absolute alcohol, saturated with nitrous anhydride, be poured over dry para-amidophenol hydrochloride, the mixture being carefully cooled by ice-water, an indigo-blue solution is at first produced which afterwards becomes brown; if sufficient ether to produce a milkiness in the liquid be then added, the whole after a short time becomes a solid mass from the separation of the diazohydrochloride. It crystallises in long colourless needles, difficultly soluble in alcohol.

**Orthodiazophenol hydrochloride**,  $\text{C}^6\text{H}^4\text{N}^2\text{Cl}$ , is similarly prepared from orthoamidophenol hydrochloride. It crystallises in colourless well-formed rhombohedrons, much more soluble in alcohol than the isomeric compound. Both these substances are extremely unstable (Schmitt, *Deut. Chem. Ges. Ber.* i. 67).

On heating a concentrated solution of sodium hydrogen sulphite, to which an ortho- or para-diazophenol salt has been added, to boiling, the diazophenol quickly dissolves without nitrogen being evolved; on cooling, the sodium salt of the product separates out, but it is better to add a concentrated solution of potassium chloride, and to recrystallise the precipitated potassium salt several times from dilute alcohol. **Potassium orthodiazophenol sulphite**,  $\text{C}^6\text{H}^4(\text{OH})\text{N}^2\text{SO}^3\text{K} + \text{OH}^2$ , thus prepared, crystallises in small golden-yellow scales; the para-diazo-derivative forms pale-yellow anhydrous needles (Schmitt a. Glutz, *Deut. Chem. Ges. Ber.* ii. 51).

**Diamidophenol**,  $\text{C}^6\text{H}^4(\text{NH}^2)_2\text{OH}$  (1 : 2 : 4).—Gauhe (*Ann. Ch. Pharm.* cxlvii. 66), by the action of hydriodic acid on  $\alpha$ -dinitrophenol, obtained the hydriodide of a base which he regards as a diamidobenzene different from the two phenylenediamines then known. It does not agree, however, in properties with the third diamidobenzene since discovered by Griess, and there is reason therefore to suppose that, although both the hydriodide and sulphate gave on analysis numbers which correspond with those required by theory for a diamidobenzene, Gauhe's product was really diamidophenol. The hydriodide forms white needles; the sulphate, magnificent rhombic plates; the hydrochloride, white needles. These salts are partially decomposed on exposure to the air; all attempts to separate the free base from them by an alkali were unsuccessful, the solution at once becoming red-brown, and after a short time depositing brown flocculi. The addition of ferric chloride caused a deep red coloration.

**Bromophenols.** **Parabromophenol**,  $\text{C}^6\text{H}^4\text{Br.OH}$  (1 : 4).—Körner (*Gazzetta chimica italiana*, 1874, iv. 387), and Fittig a. Mager (*Deut. Chem. Ges. Ber.* vii. 1176) have prepared this compound from parabromaniline (m.p.  $66.4^{\circ}$  Körner,  $63^{\circ}$  Fittig a. Mager). Parabromaniline nitrate, mixed with an excess of nitric acid, was treated with nitrous anhydride; the resulting diazobromobenzene nitrate was converted into sulphate by the addition of sulphuric acid, and the sulphate precipitated by alcohol and ether; the crystallised diazobenzene sulphate was then dissolved in a large quantity of water, and the solution gently heated. The bromophenol produced was extracted with ether and purified by distillation. Parabromophenol is also obtained by distilling bromosalicylic acid with burnt lime (Huebner a. Brenken, *ibid.* vi. 170). The product is an oil of which the greater part distils over at about  $235^{\circ}$ , and is easily converted by cooling into a crystalline mass; it may be purified by pressing and recrystallisation from chloroform. Huebner a. Brenken have shown that parabromophenol may be readily prepared from phenol by the following process:—The calculated quantity of bromine dissolved in 200 grams of glacial acetic acid is added to a well-cooled solution of 100 grams of phenol in 300 of acetic acid; a strong current of carbonic anhydride is then passed through the liquid to remove the hydrobromic acid; and subsequently the solution is cooled in a mixture of ice and salt. The crystals which separate after a time are removed by filtration in a vacuum-filter, pressed until quite dry and as free as possible from acetic acid, and then several times carefully fused and again allowed to solidify, in order to remove adherent hydrobromic acid; after which they may be distilled, the portion boiling at  $235^{\circ}$ – $236^{\circ}$  being collected apart and several times recrystallised from chloroform.

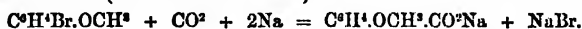
Parabromophenol crystallises in large, colourless, transparent (probably) monoclinic



crystals, which become pink on long exposure to the air; it melts at  $66.4^{\circ}$  (Körner),  $63^{\circ}$ - $64^{\circ}$  (Huebner, Fittig a. Mager), and distils, undergoing scarcely any decomposition, at  $238^{\circ}$  (Fittig),  $235^{\circ}$ - $236^{\circ}$  (Huebner a. Brenkon). It dissolves in a large quantity of cold water, and more readily in hot water; it is easily soluble in alcohol, chloroform, and acetic acid. On nitration it yields Brunck's parabromonitrophenol, melting at  $88^{\circ}$  (Huebner a. Brenken, Körner), or bromodinitrophenol, melting at  $76^{\circ}$  (Körner, Armstrong), according to the amount of nitric acid employed. When fused with potassium hydrate it yields resorcin free from its isomerides (Fittig a. Mager).

*Metabromophenol*,  $\text{C}^6\text{H}^4\text{Br.OH}$  (1 : 3), has been obtained by Körner (*loc. cit.*) and by Wurster a. Nölting (*Deut. Chem. Ges. Ber.* vii. 904) from metabromaniline by Griess's method. It is an oil boiling at  $227^{\circ}$ - $229^{\circ}$  (W. u. N.). According to Wurster a. Nölting, it is converted into resorcin on fusion with potassium hydrate. On treatment with bromine in excess it yields tetrabromophenol, and with nitric acid furnishes, amongst other products, a dinitrobromophenol melting at  $91.5^{\circ}$  (Körner).

Metabromophenol, according to Körner's observations, may also be produced by the direct action of bromine on phenol, but it is not known at present what are the circumstances favourable to its production, nor indeed even whether it is always present in the crude bromophenol. Körner converted the bromophenol which he prepared by passing a current of air laden with bromine into cooled phenol (1st *Suppl.* 907) into the methyl ether,  $\text{C}^6\text{H}^4\text{Br.O.CH}_3$ , by acting upon its potassium derivat with methyl iodide, and from this he obtained, by the action of carbonic anhydride and sodium, a methoxybenzoic acid identical with that prepared by Graebe and Schultzen from ordinary oxybenzoic acid ( $\text{OH} : \text{COOH} = 1 : 3$ ):



By the action of sodium and methyl iodide on the same methyl-bromophenol a methyl-cresol was obtained,  $(\text{C}^6\text{H}^4\text{Br.OCH}_3 + \text{CH}_3\text{I} + 2\text{Na} = \text{C}^6\text{H}^4\text{CH}_3.\text{OCH}_3 + \text{NaBr} + \text{NaI})$ , also yielding methoxybenzoic acid on oxidation (*Bull. de l'Acad. Belg.* 1867; *Zeitschr. f. Chem.* 1868, 326). In his recent memoir (*Gazzetta chimica italiana*, iv. 389) Körner states that he has re-examined specimens of the methoxybenzoic acid and methyl cresol prepared in 1866, which he had preserved, and convinced himself anew of the correctness of his observations; at the same time he mentions that he was unable to obtain similar results with a bromophenol prepared under conditions apparently identical with those previously observed by him in its preparation.

*Orthobromophenol*,  $\text{C}^6\text{H}^4\text{Br.OH}$  (1 : 2), has been prepared by Körner (*loc. cit.*) from orthobromaniline by Griess's method, and by the decomposition of the platinobromide of the diazophenol formed from orthoamidophenol. It is a colourless oil. On nitration it is ultimately converted into bromo- $\alpha$ -dinitrophenol (Körner; Armstrong).

Orthobromophenol is always produced by the action of bromine on phenol, and the acetic acid solution which drains from the crystals of parabromophenol prepared by Huebner a. Brenken's method contains it in considerable quantity.

**Chlorophenols.** *Parachlorophenol*,  $\text{C}^6\text{H}^4\text{Cl.OH}$  (1 : 4), which was first obtained in a state of purity by the action of sulphuric chloride,  $\text{SO}^2\text{Cl}_2$ , on phenol, is formed when the platinochloride of paradiaphenol is submitted to distillation (Schmitt, *Deut. Chem. Ges. Ber.* i. 67), and from parachloraniline (m. p.  $70^{\circ}$ ) by Griess's method (Beilstein a. Kurbatow, *ibid.* vii. 1395). It may also readily be prepared by passing chlorine into phenol, mixed with sufficient water to prevent its solidifying and cooled with ice, until it has increased in weight by the calculated amount; the product is washed with water and a little dilute potassium hydrate solution to remove hydrochloric acid, dried by calcium chloride and anhydrous cupric sulphate, and then fractionally distilled. The portion boiling at  $215^{\circ}$ - $220^{\circ}$  solidifies at about  $0^{\circ}$ , but melts again at  $8^{\circ}$ ; by allowing the liquid portion to drain away, however, it is possible to raise the melting point almost to that observed by Dubois (Petersen a. Baehr-Predari, *Ann. Ch. Pharm.* clvii. 123).

Parachlorophenol melts at  $41^{\circ}$  (Dubois),  $37^{\circ}$  (Beilstein a. Kurbatow), and boils at  $218^{\circ}$  (Petersen a. Predari),  $217^{\circ}$  (Beilstein a. Kurbatow). When fused with potassium hydrate, the chlorophenol boiling at  $218^{\circ}$  prepared from phenol furnishes chiefly hydroquinone and traces of resorcin, according to Petersen a. Baehr-Predari (*loc. cit.* and *Deut. Chem. Ges. Ber.* vii. 61), but Faust states that resorcin only is obtained (*ibid.* vi. 1022). Parachlorophenol yields ordinary dichlorobenzene (m. p.  $53^{\circ}$ , b. p.  $172^{\circ}$ ) when distilled with phosphorus pentachloride (Beilstein a. Kurbatow). Dilute nitric acid converts it into parachloronitrophenol melting at  $86.5^{\circ}$  (Beilstein a. Kurbatow). *Methyl-parachlorophenol*,  $\text{C}^6\text{H}^4\text{Cl.O.CH}_3$ , boils at  $198^{\circ}$ - $202^{\circ}$ , and does not solidify at  $-18^{\circ}$ ; *ethyl-parachlorophenol*,  $\text{C}^6\text{H}^4\text{ClO.C}^2\text{H}_5$ , melts at  $21^{\circ}$  and boils at  $210^{\circ}$ - $212^{\circ}$  (Beilstein a. Kurbatow).

*Metachlorophenol*,  $\text{C}^6\text{H}^4\text{Cl.OH}$  (1 : 3), is obtained by Griess's method from meta-

chloraniline (from dinitrobenzene); it is an oil boiling at  $214^{\circ}$  (Beilstein a. Kurbatow, *loc. cit.*)

**Orthochlorophenol**,  $C^6H^4Cl.OH$  (1 : 2).—Beilstein a. Kurbatow (*loc. cit.*) have prepared this modification from orthochloraniline by Griess's method, and it was previously obtained by Faust a. Müller (*Deut. Chem. Ges. Ber.* v. 777; *Ann. Ch. Pharm.* clxxiii, 303), by distilling orthodiazophenol platinochloride. On passing chlorine into 500 grams of phenol without cooling until the weight is increased by 200 grams, and fractioning the product, which boils at  $175^{\circ}$ – $220^{\circ}$ , a portion is obtained boiling constantly at  $175.5^{\circ}$ – $177^{\circ}$ , consisting of orthochlorophenol (Faust a. Müller, *loc. cit.*) It is a colourless, oily liquid, which has a peculiar unpleasant odour, and does not solidify at  $-15^{\circ}$  (Faust a. Müller). According to Kramers (*Ann. Ch. Pharm.* clxxiii, 331) the yield of orthochlorophenol is about one-third of the weight of phenol employed; he describes it as a colourless oil, boiling constantly at  $176^{\circ}$ – $177^{\circ}$  under a pressure of 760 mm., the mercury-column in the thermometer being wholly immersed in the vapour. On cooling it to  $-12^{\circ}$ , he found that it solidifies to a mass exactly resembling pure crystalline phenol; when removed from the refrigerating mixture it fuses, and a thermometer immersed in the fusing mass exhibits constantly the temperature  $7^{\circ}$ . When fused with potassium hydrate, orthochlorophenol yields pyrocatechin, the conversion taking place far more readily than that of parachlorophenol into resorcin (Faust a. Müller, *loc. cit.*; Petersen, *Deut. Chem. Ges. Ber.* vi. 368). By the action of dilute nitric acid it furnishes orthochloroparanitrophenol, melting at  $110^{\circ}$ – $111^{\circ}$ , and orthochlorororthonitrophenol, melting at  $70^{\circ}$  (Faust a. Müller; Beilstein a. Kurbatow). When distilled with phosphorus pentachloride it is converted into orthodichlorobenzene, boiling at  $179^{\circ}$ ; sp. gr. 1.3278 at  $0^{\circ}$  (Beilstein a. Kurbatow). **Ethyl-orthochlorophenol**,  $C^6H^4Cl.O.C^2H^5$ , is a liquid boiling at  $208^{\circ}$ – $208.5^{\circ}$  (Beilstein a. Kurbatow).

**Pentachlorophenol**,  $C^6Cl^5.OH$ . **Perchlorophenol**.—To prepare this compound, chlorine is passed into a mixture of 3 pts. of phenol and 1 pt. of antimonious chloride, which is heated at first on the water-bath and afterwards in a salt-bath, until all action ceases. The resulting mass is boiled with sodium hydrate solution, and the hot filtrate supersaturated with hydrochloric acid; the precipitated crude pentachlorophenol is then distilled in a current of superheated steam ( $180^{\circ}$ – $200^{\circ}$ ), and recrystallised from petroleum spirit (Merz a. Weith, *ibid.* v. 458).

Pentachlorophenol crystallises in long colourless glistening needles, and is very soluble in alcohol and ether, moderately soluble in benzene, and slightly soluble in cold petroleum spirit. It melts at  $186^{\circ}$ – $187^{\circ}$ . When cold it has no odour, but when heated it has an intensely sharp odour and causes coughing. Pentachlorophenol dissolves, although slowly, in cold solutions of potassium or sodium hydrate; it is almost entirely precipitated, however, from dilute alkaline solutions by carbonic anhydride. **Potassium pentachlorophenol**,  $C^6Cl^5.OK$ , crystallises from ether-alcohol in long white needles; it is easily soluble in anhydrous alcohol, and even in ether. **Sodium pentachlorophenol** closely resembles the potassium-derivative. **Ammonium pentachlorophenol**,  $C^6Cl^5.ONH^4$ , crystallises from a hot ammoniacal solution in very long thin pliable needles; it scarcely dissolves in water, although it is readily soluble in alcohol. Pentachlorophenol is only very slowly attacked by nascent hydrogen from sodium-amalgam and water. Concentrated nitric acid converts it, even in the cold, into tetrachloroquinone:

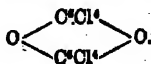


When distilled with phosphorus pentachloride it furnishes hexachlorobenzene. Potassium hydrate has scarcely any action below  $200^{\circ}$ ; at  $230^{\circ}$ – $240^{\circ}$  humus-like substances are largely produced, free from chlorine and insoluble in water; the alkaline solution contains a large quantity of oxalate.

Pentachlorophenol is decomposed on distillation, hydrochloric acid being evolved, and tetrachlorophenylene oxide is produced:



Potassium pentachlorophenol undergoes a corresponding decomposition when heated. The product is powdered and washed with alcohol, crystallised from boiling nitrobenzene, and then several times recrystallised from hot turpentine. **Tetrachlorophenylene oxide** is scarcely dissolved by alcohol, ether, chloroform, or carbon sulphide, but is readily soluble in boiling nitrobenzene, and moderately soluble in hot turpentine. It forms broad white needles like benzoic acid. It melts at about  $320^{\circ}$ , and distils undecomposed at a temperature far above that at which mercury boils. On account of its high melting and boiling points, Merz a. Weith are inclined to represent it by the formula:



It is not attacked by sodium-amalgam and water, or by phosphorus pentachloride—even at 240°–250°. Boiling concentrated nitric acid very slowly decomposes it, chlorine and carbonic anhydride being evolved.

**Iodophenols** (Lobanoff, *Deut. Chem. Ges. Ber.* vi. 1251). The iodophenol prepared by Körner's method (1st *Suppl.* 909) is a mixture of the three isomeric mono-iodophenols. When it is distilled in a current of steam, first a liquid iodophenol passes over, then a solid iodophenol, and finally tri-iodophenol; and the residue contains a considerable quantity of the latter, which may be extracted by alcohol. The third modification, which is easily soluble in water, is found in part in the aqueous solution from which the crude iodophenol is precipitated, in part in the aqueous distillate, and in part in the alcoholic solution from which the tri-iodophenol crystallises. In order to separate it, these solutions are rendered alkaline with potassium hydrate, concentrated by evaporation, and then supersaturated with hydrochloric acid. The precipitated iodophenol is purified by recrystallisation. It crystallises from ether in needles, from alcohol in large six-sided plates, and from carbon sulphide in short thick prisms; it dissolves well in water and ether, and very easily, in alcohol and carbon sulphide. It melts at 89°. The second solid iodophenol, which melts at 64°–66°, is difficultly soluble in water, but easily soluble in alcohol and ether, and crystallises in flat glistening needles. The liquid iodophenol does not solidify at –23°. Iodine is not separated by chlorine or nitric acid from the iodophenol melting at 89°, or from that which melts at 64°–66° by chlorine; nitric acid, however, liberates iodine from this modification. The liquid iodophenol is decomposed both by chlorine and by nitric acid.

The constitution of these compounds has not yet been determined, but a comparison of Lobanoff's results with those of Körner renders it probable that the modification melting at 64°–66° is *paraiodophenol* (1 : 4), identical with Körner's *orthoiodophenol*, whilst that melting at 89° is *metaiodophenol* (1 : 3), identical with Körner's *paraiodophenol* from dinitrobenzene; the liquid modification being *orthoiodophenol* (1 : 2), identical with Körner's *metaiodophenol*.

**Nitrophenols.** *Paranitrophenol*,  $C^6H^4(NO^2)OH$  (1 : 4).—The volatile non-modification of nitrophenol, which has long been known as *ortho-* and *isonitrophenol*, has recently been shown to be a member of the *para* series. It is produced: 1. When  $\alpha$ -nitrochlorobenzene (m. p. 85°) from chlorobenzene is heated with potassium hydrate solution at 130° (Engelhardt a. Latschinow, *Deut. Chem. Ges. Ber.* iii. 423). 2. When  $\alpha$ -nitrobromobenzene (m. p. 125°) from bromobenzene is heated with potassium hydrate solution (von Richter, *ibid.* iv. 460). 3. By heating nitroacetanilide from acetanilide with concentrated sodium-hydrate solution until ammonia ceases to be evolved (Wagner, *ibid.* vii. 76). 4. By decomposing diazonitrobenzene nitrate, prepared from the nitraniline obtained from acetanilide by boiling with water (Fittig, *ibid.* vii. 280). 5. By dry distillation of nitrosaliclic acid mixed with powdered pumice (Schmitt a. Cook, *Kekulé Org. Chem.* iii. 41). 6. By oxidation of nitrosophenol (Bayer, *Deut. Chem. Ges. Ber.* vii. 965).

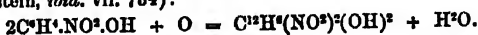
Pure paranitrophenol melts at 114°. Salkowski (*ibid.* vii. 45) has converted it into anisic or methyl-*para*-oxybenzoic acid in the following manner:—Silver paranitrophenol was treated with methyl iodide, and the resulting methyl-paranitrophenol or paranitro-anisol,  $C^6H^4.NO^2.OCH^3$ , reduced to methyl-*para*-amidophenol or *para*-amidoanisol; the latter was then converted by Griess's method into the *dinzo*-perbromide, which was distilled with lime. Methyl-*para*-bromophenol was then obtained, which, when acted upon by methyl-iodide and sodium, gave methyl-*para*-cresol,  $C^6H^4.OH^2.OCH^3$ , yielding anisic acid,  $C^6H^4.OCH^3.CO^2H$ , on oxidation with potassium dichromate and glacial acetic acid.

Salkowski (*ibid.* 1008) also found that when the *paradiazoo*anisol sulphate from *para*-amidoanisol, prepared as above described, is heated with water, hydroquinone is produced. The *paradiazoo*anisol sulphate and nitrate obtained by the action of nitrous acid on *para*-amidoanisol sulphate or nitrate in presence of a small quantity of water are remarkably stable substances; on concentrating the solution by slow evaporation on the water-bath at a low temperature, they separate in broad flat needles. They are only very slowly decomposed when boiled with water or dilute acids; the decomposition is complete, however, after heating for some hours at 140° in sealed tubes, position is complete, however, after heating for some hours at 140° in sealed tubes, the greater part being converted into a brown viscid substance—probably a methyl ether of hydroquinone—and only the smaller part into hydroquinone. On heating *para*-nitroanisol with aqueous ammonia at 170°–200°, *paranitraniline* or *paranitro*-*amido*benzene, identical with that which is obtained from acetanilide, is formed (Salkowski, *Ann. Ch. Pharm.* lxxiv. 281). When distilled with phosphorus pentachloride, *paranitrophenol* yields  $\alpha$ -chloronitrobenzene (m. p. 85°) according to Engelhardt a. Latschinoff (*Deut. Chem. Ges. Ber.* iii. 200). On digestion with fuming sulphuric acid, it is converted into *paranitrophenolsulphonic acid* (Post, *ibid.* v. 852; vi. 396).

**Metanitrophenol**,  $C^6H^4(NO^2)OH$  (1 : 3), is produced on heating the diazonitrobenzene nitrate prepared from the nitraniline from ordinary dinitrobenzene (m. p.  $87^\circ$ ) with water. The solution is filtered from the resin, and shaken with ether; on distilling off the ether, an oil remains, which gradually crystallises when exposed over sulphuric acid. It may be purified by recrystallisation from boiling water or alcohol. Metanitrophenol forms hard, compact, almost colourless crystals, melting at  $95^\circ-96^\circ$ ; it is moderately soluble in cold water, and readily soluble in boiling water and alcohol. It scarcely volatilises in a current of steam. Metanitrophenol has a great tendency to remain liquid; when only slightly warmed with water it melts, and always separates from the aqueous solution as an oil, which may remain for days under the liquid without solidifying, but at once crystallises on the addition of a trace of the solid. Also when cold alcohol is poured on the crystals they immediately liquefy, and it regularly separates from the alcoholic solution as an oil (Fittig a. Bantlin, *ibid.* vii. 179). Potassium metanitrophenol crystallises in magnificent long glistening needles, which appear deep red so long as they are surrounded by liquid, but orange after drying; it is very soluble in water and alcohol.

**Orthonitrophenol**,  $C^6H^4(NO^2)OH$  (1 : 2).—This modification, commonly known as volatile nitrophenol, is produced:—1. When the  $\gamma$ -nitrobromobenzene (m. p.  $37^\circ-38^\circ$ ), formed simultaneously with  $\alpha$ -nitrobromobenzene on nitration of bromobenzene, is heated with potassium hydrate solution in sealed tubes (Zincke a. Walker, *ibid.* v. 114); and 2. When the corresponding nitrochlorobenzene from chlorobenzene is similarly treated (Engelhardt a. Latschinoff, *ibid.* iii. 423).

When the orthonitranisol,  $C^6H^4.NO^2.OCH^3$ , from orthonitrophenol, is heated with aqueous ammonia in sealed tubes at about  $200^\circ$ , it is converted into nitraniline (m. p.  $61^\circ$ ), identical with that obtained by the action of ammonia on  $\gamma$ -nitrobromobenzene (m. p.  $37^\circ-38^\circ$ ) (Salkowski, *Ann. Ch. Pharm.* clxxiv. 277). It furnishes the corresponding nitrochlorobenzene when distilled with phosphorus pentachloride (Engelhardt a. Latschinoff, *Deut. Chem. Ges. Ber.* iii. 200). When acted upon by nitric acid it yields two isomeric dinitrophenols (Huebner a. Schneider, *Ann. Ch. Pharm.* clxvii. 89)\*. Similarly, when acted upon by chlorine, bromine, and sulphuric acid, it furnishes two isomeric chloronitro-, bromonitro- and sulphonitrophenols—nitrophenol-sulphonic acids (Armstrong, Prevost a. Brown, *Deut. Chem. Ges. Ber.* vii. 922); and, according to Busch (*ibid.* 460) a mixture of two isomeric iodonitrophenols on treatment with iodine. When oxidised by permanganic acid it is converted into dinitrophenol (Goldstein, *ibid.* vii. 734):



**Dinitrophenols**.— $\alpha$ -Dinitrophenol,  $C^6H^3(NO^2)_2OH$  (1 : 2 : 4)\*, is obtained in a state of purity by the action of nitric acid on paranitrophenol (1 : 4), and also on warming dinitroamidophenol or picramic acid with ethyl nitrite, and together with  $\beta$ -dinitrophenol by the action of nitric acid on orthonitrophenol (1 : 2). It is also produced when dinitrochlorobenzene (m. p.  $50^\circ$ ) from chlorobenzene, and dinitrobromobenzene (m. p.  $72^\circ$ ) from bromobenzene, are heated with potassium or sodium hydrate solution (Clemm, *J. pr. Chem.* [2], i. 145; Engelhardt a. Latschinoff, *Deut. Chem. Ges. Ber.* iii. 97). When distilled with phosphorus pentachloride, on the other hand,  $\alpha$ -dinitrophenol yields dinitrochlorobenzene melting at  $48^\circ-49^\circ$  (Clemm, Engelhardt a. Latschinoff, *loc. cit.*). The dinitraniline (m. p.  $175^\circ$ ) obtained by heating this dinitrochlorobenzene with ammonia, which is identical with that produced on similarly treating  $\alpha$ -dinitranisol,  $C^6H^3(NO^2)_2.OCH^3$ , is converted into ordinary dinitrobenzene (m. p.  $87^\circ$ ) by the action of ethyl nitrite (Rudnew, *Deut. Chem. Ges. Ber.* iv. 409; Salkowski, *Ann. Ch. Pharm.* clxxiv. 263).

Pure  $\alpha$ -dinitrophenol melts at  $113^\circ-114^\circ$ ; it crystallises from water in rectangular striated yellowish-white plates, which are usually united in fern-like forms. Characteristic of  $\alpha$ -dinitrophenol is the circumstance that its metallic derivatives are capable of crystallising with varying amounts of water (*vide*  $\beta$ -dinitrophenol). Ordinary trinitrophenol (picric acid) alone is produced when  $\alpha$ -dinitrophenol is treated with nitric acid (Huebner a. Schneider).

$\alpha$ -Dinitrophenetol,  $C^6H^3(NO^2)_2.OC^2H^5$ , from silver  $\alpha$ -dinitrophenol and ethyl iodide, melts at  $84^\circ$  (Salkowski, *loc. cit.*)

$\beta$ -Dinitrophenol,  $C^6H^3(NO^2)_2OH$  (1 : 2 : 6), is formed, together with  $\alpha$ -dinitrophenol, on nitrating orthonitrophenol (1 : 2). The following are the details of its preparation as given by Huebner a. Schneider, by whom it was first made known (*Ann. Ch. Pharm.* clxvii. 80). The orthonitrophenol, in quantities not exceeding 20–25 grams, is placed in a capacious flask together with an equal weight of nitric acid (sp. gr. 1.36), and the mixture is carefully warmed on the water-bath until the reaction commences, which

\* In this representing the constitution of the phenol-derivatives the OH-group is throughout this article supposed to occupy the position 1.

is extremely violent, but of short duration. The product, which is at first oily but soon solidifies, is a mixture of the two dinitrophenols with trinitrophenol and unattacked nitrophenol. After being washed with cold water until free from acid, it is introduced into a flask with water, and heated in a current of steam until the ortho-nitrophenol is entirely removed; it is then boiled with water and an excess of barium carbonate, the solution filtered, and the residue several times extracted with boiling water. As soon as the liquid has cooled to 40°, the almost pure  $\beta$ -salt which separates is rapidly removed by filtration; on further cooling the filtrate yields a mixture of the  $\alpha$ - and  $\beta$ -salt, which is also filtered off, and the mother-liquor then contains barium di- and trinitrophenol. Barium  $\beta$ -dinitrophenol is very slightly soluble in water at 30°–40°, but somewhat more soluble in boiling water; the  $\alpha$ -salt, however, is easily soluble under these conditions. The two salts may therefore be separated without difficulty by treatment with warm water; but, according to Huebner a. Schneider, the separation is greatly facilitated by the use of 90 p.c. alcohol, which dissolves only traces of the  $\beta$ -salt, but in which the  $\alpha$ -salt dissolves with moderate readiness. Salkowski (*Ann. Ch. Pharm.* clxiv. 270) converts the mixed barium salts into potassium salts by potassium carbonate, and removes the greater part of the  $\alpha$ -salt by crystallisation; the mother-liquor is then heated to 40°–50°, and precipitated by barium chloride, whereby only  $\beta$ -barium dinitrophenol is thrown down. This may be purified by a single recrystallisation after washing with cold water; or, in the case of large quantities, it is converted into potassium salt, and this is recrystallised. Körner (*Gazzetta chimica italiana*, 1874, 325) crystallises the potassium salts from water, and then exposes the mixture to the sun's rays for some days; the  $\alpha$ -salt crumbles down to a powder, and may be separated mechanically from the  $\beta$ -salt, which is purified by recrystallisation.

$\beta$ -Dinitrophenol crystallises from water in fine, short, pale-yellow needles, pointed at the ends; from chloroform it separates in long coarse needles. It is more soluble in cold water, though less soluble in boiling water, than  $\alpha$ -dinitrophenol; it is very soluble in chloroform, benzene, ether, and boiling alcohol. It melts at 63°–64°. The dinitroaniline (m. p. 138°) obtained on heating  $\beta$ -dinitroanisole,  $\text{C}_6\text{H}_4(\text{NO}_2)_2\text{OCH}_3$ , from  $\beta$ -dinitrophenol with aqueous ammonia at 130°, is converted into ordinary dinitrobenzene (m. p. 87°) when heated with ethyl nitrite (Salkowski, *Ann. Ch. Pharm.* clxiv. 274). The dinitroaniline from  $\beta$ -dinitrophenol is much less readily decomposed by ethyl nitrite than that derived from the  $\alpha$ -dinitrophenol; in the latter case it is merely necessary to heat the substances together in a flask, but in the former they must be digested in sealed tubes at 120° (Salkowski). Concentrated nitric acid converts  $\beta$ -dinitrophenol into ordinary trinitrophenol (Huebner a. Schneider).

The metallic derivatives of  $\beta$ -dinitrophenol differ considerably in composition, appearance, and solubility from those of  $\alpha$ -dinitrophenol; this will be evident on inspection of the table on page 910.

$\beta$ -Dinitroanisole,  $\text{C}_6\text{H}_4(\text{NO}_2)_2\text{OCH}_3$ , crystallises from alcohol in colourless needles, melting at 116°, soluble in 64.2 pts. of 95 volume p.c. alcohol at 21° ( $\alpha$ -dinitroanisole melts at 87°, and dissolves in 110 pts. of alcohol at 21°).  $\beta$ -Dinitrophenetole,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OC}_2\text{H}_5$ , also crystallises in colourless needles which melt at 57°–58° (Salkowski, *Ann. Ch. Pharm.* clxiv. 273).

*Trinitrophenol*,  $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$  (1 : 2 : 4 : 6), is obtained by nitration of both  $\alpha$ - and  $\beta$ -dinitrophenol. It is also formed when trinitrochlorobenzene (m. p. 82°–83°) is boiled with sodium hydrate or carbonate solution (Engelhardt a. Latschinoff, *Deut. Chem. Ges. Ber.* iii. 98; Clemm, *J. pr. Chem.* [2] i. 145). According to E. a. L. the conversion of trinitrochlorobenzene to trinitrophenol is effected by boiling with water, but Clemm denies this. Trinitrochlorobenzene is readily obtained by the action of phosphorus pentachloride on trinitrophenol. An intimate mixture of at most 100 grams of the latter with 200 grams of chloride is very cautiously warmed in a large retort or flask connected with a wide reversed condenser. As soon as the mass begins to liquefy, the source of heat is removed; the reaction which then takes place is exceedingly violent. The liquid product is afterwards gently boiled for some time the phosphorus oxychloride is then distilled off, and the mass thrown into a large quantity of water. When solid, it is pulverised, washed with ether, and recrystallised from alcohol, and finally from petroleum spirit, in which it is only very slightly soluble, however. The trinitroaniline obtained by heating trinitrochlorobenzene (Clemm) or trinitroanisole,  $\text{C}_6\text{H}_4(\text{NO}_2)_3\text{OCH}_3$  (Salkowski, *Deut. Chem. Ges. Ber.* iv. 873), with ammonia is not decomposed by ethyl nitrite even at 160° (v. Meyer, *Ann. Ch. Pharm.* clxv. 187).

The chlorodinitrophenol produced by Stenhouse's reaction by heating trinitrophenol with iodine chloride and water (1st Suppl. 914) consists of chloro- $\alpha$ -dinitrophenol (m. p.

Metallic derivatives of $\alpha$ -dinitrophenol	Metallic derivatives of $\beta$ -dinitrophenol
<p>a. <math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Ba} + 7\text{H}_2\text{O}</math> Golden-yellow prismatic needles.</p> <p>b. <math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Ba} + 6\text{H}_2\text{O}</math> Fine pale-yellow needles.</p> <p>c. <math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Ba} + 5\text{H}_2\text{O}</math> Orange-red prisms. Solubility 1 : 320 at <math>7^\circ</math>.</p>	<p><math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Ba} + \text{H}_2\text{O}</math> Fine golden-yellow striated needles. Solubility 1 : 555 at <math>7^\circ</math>.</p>
<p>a. <math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{OK} + \text{H}_2\text{O}</math> Dark-yellow prisms.</p> <p>b. <math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{OK} + \frac{1}{2}\text{H}_2\text{O}</math> Pale-yellow six-sided needles. Solubility 1 : 59.2 at <math>7^\circ</math>.</p>	<p><math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{OK}</math> Flat red needles which exhibit magnificent trichroism. Solubility 1 : 59.3 at <math>6^\circ</math>.</p>
<p><math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{ONa} + \text{H}_2\text{O}</math> Fine pale-yellow needles.</p>	<p><math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{ONa} + 3\text{H}_2\text{O}</math> Brilliant red long needles.</p>
<p>a. <math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Mg} + 12\text{H}_2\text{O}</math> Coarse pale-yellow prisms.</p> <p>b. <math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Mg} + 9\text{H}_2\text{O}</math> Pale-yellow prismatic needles.</p>	<p><math>[\text{C}^6\text{H}_3(\text{NO}_2)_2\text{O}]^+\text{Mg} + 6\text{H}_2\text{O}</math> Coarse red prismatic needles.</p>
<p><math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{OPbOH} + 2\text{H}_2\text{O}</math> Golden-yellow lance-shaped needles.</p>	<p><math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{OPbO}</math> <math>\text{C}^6\text{H}_3(\text{NO}_2)_2\text{OPb}</math> Fine orange needles.</p>

$110^\circ$ – $111^\circ$ ) mixed with a relatively small quantity of Dubois' parachloro- $\beta$ -dinitrophenol (Petersen, *Deut. Chem. Ges. Ber.* vi. 368; Armstrong, *ibid.* 650). When trinitrophenol is similarly acted upon by iodine bromide, it yields bromo- $\alpha$ -dinitrophenol melting at  $117^\circ$  (Armstrong, *loc. cit.*)

By heating with acetic anhydride trinitrophenol is converted into acetyl-trinitrophenol,  $\text{C}^6\text{H}_2(\text{NO}_2)_3\cdot\text{O}\cdot\text{C}^6\text{H}_3\text{O}$ ; it is a crystalline pale-yellow substance, which melts at  $76^\circ$ – $76^\circ$  (Tommasi a. David, *Compt. rend.* lxxvii. 207).

**Diamidodinitrophenol**,  $\text{C}^6\text{H}_3(\text{NO}_2)(\text{NH}_2)_2\text{OH}$  (1 : 2 : 4 : 6).—This compound is obtained by reducing trinitrophenol with aqueous ammonium sulphide (Griess, *Ann. Ch. Pharm.* cliv. 202). To prepare it, pulverised trinitrophenol is mixed with a large excess of dilute aqueous ammonia and a rapid current of hydrogen sulphide then passed in, the mixture being shaken from time to time. The conversion is complete, and the passage of the gas must be stopped so soon as very dilute hydrochloric acid fails to produce a precipitate in a portion of the solution which has previously been concentrated and filtered from the separated sulphur. The liquid is then concentrated somewhat by evaporation, filtered from the sulphur, and supersaturated with acetic acid. The brownish needles of diamidodinitrophenol which separate are obtained perfectly pure after a single recrystallisation from water to which a little animal charcoal is added. Diamidodinitrophenol crystallises in long dark-yellow needles or narrow plates. It is somewhat more soluble in alcohol than in water, but very slightly soluble in ether. The air-dry substance contains a molecule of water of crystallisation, which is readily given off above  $100^\circ$ .

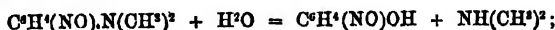
Diamidodinitrophenol has far stronger basic properties than amidodinitrophenol (picramic acid), which dissolves only in concentrated acids, the resulting compounds being decomposed on the addition of water. Diamidodinitrophenol is soluble even in very dilute solutions of the mineral acids, forming stable compounds; like amidodinitrophenol, it does not unite with organic acids, however. *Diamidodinitrophenol sulphate*,  $[\text{C}^6\text{H}_3(\text{NH}_2)_2(\text{NO}_2)\text{OH}]^+\cdot\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$ , crystallises in long yellowish needles or columns, and is difficultly soluble even in boiling water. *Diamidodinitrophenol hydrochloride* forms delicate four-sided plates usually of a greenish colour. It is very soluble in cold water and alcohol, but is separated from the latter solution in crystals by ether. Platinum chloride produces no precipitate, even in very concentrated solutions of this salt.

The metallic derivatives of diamidodinitrophenol are far less stable than those of amidodinitrophenol, and undergo oxidation when exposed to the air in a moist state.

Those which are dissolved by water are more soluble than the corresponding amidodinitrophenol derivatives. *Barium diamidonitrophenol*,  $[\text{C}_6\text{H}_3(\text{NH})_2(\text{NO})_2\text{O}]^{2+}\text{Ba} + 2\text{H}_2\text{O}$ , separates in ruby-red needles on the addition of barium chloride to a solution of ammonium diamidonitrophenol. If recrystallised from water, in which it is moderately soluble, it is obtained in almost black glistening prisms. Silver diamidonitrophenol separates as a reddish-yellow precipitate which rapidly blackens on the addition of silver nitrate to a solution of ammonium diamidonitrophenol. The zinc derivative resembles the silver derivative, but is far more stable. Basic lead acetate produces a reddish-brown precipitate in an aqueous solution of diamidonitrophenol.

The formation of diamidonitrophenol is preceded by that of amidodinitrophenol, according to Griess; but his experiments show that, when the reduction of trinitrophenol takes place in an alcoholic solution, as in the preparation of amidodinitrophenol by Girard's method, it has but little tendency to extend to more than one of the three nitro-groups. Aqueous ammonium sulphide scarcely acts upon diamidonitrophenol in the cold, but when heated to boiling converts it completely into a blue-black, neutral, amorphous body, which is insoluble in all the ordinary solvents, but is dissolved by strong warm sulphuric acid (Griess).

**Nitrosophenols.** *Paranitrosophenol*,  $\text{C}_6\text{H}_4(\text{NO})\text{OH}$  (1 : 4) (Baeyer a. Caro, *Deut. Chem. Ges. Ber.* vii. 983), is produced when nitrosodimethylaniline is boiled with sodium hydrate solution :



and by the action of nitrous acid on phenol.

Baeyer a. Caro prepare nitrosodimethylaniline by adding 100 pts. of amyl nitrite to a mixture of 50 pts. of dimethylaniline with 100 pts. of concentrated hydrochloric acid and 750 pts. of a mixture of 1 vol. of hydrochloric acid with 2 vols. of alcohol, which is well cooled with ice. After a short time yellow needles of nitrosodimethylaniline hydrochloride separate; as soon as these no longer increase in quantity, the mass is thrown on a vacuum-filter, and washed with ether-alcohol.

To prepare the nitrosophenol, a mixture of 90 pts. water with 10 pts. sodium hydrate solution (sp. gr. 1.25), is heated to boiling in a flask connected with a reversed condenser, and 2 pts. nitrosodimethylaniline hydrochloride is gradually added, care being taken each time to await the disappearance of the oily drops of the base before adding a fresh quantity of the salt. The boiling is continued until the dark greenish-yellow colour has entirely disappeared and changed to reddish-yellow. The greater part of the dimethylamine passes over during the boiling, and should be collected in hydrochloric acid. To obtain the nitrosophenol the solution is well cooled, rendered slightly acid with sulphuric acid, and extracted with ether; on distilling off the ether it remains in the form of a brown crystalline mass.

Phenol is converted into nitrosophenol in the following manner:—5 pts. of phenol and 20 pts. of potassium nitrite are dissolved in 1,000 pts. of water, and the solution cooled as well as possible with ice-water; 10–12 pts. of ordinary acetic acid, diluted with 10 vols. of water, is then added little by little and with constant shaking. After 12–16 hours the brown liquid is filtered to separate a small quantity of resin, and extracted with ether; in order, however, to avoid the action of any excess of phenol, and of the nitrous acid present, on the nitrosophenol, which would occur on distilling off the ether, concentrated sodium hydrate solution is added. The mass of sodium nitrosophenol which separates is spread upon porous plates; when dry it is dissolved in water, the nitrosophenol is separated by sulphuric acid, and after being slightly washed, it is rapidly dissolved in hot water; the solution is then filtered, cooled, and extracted with ether. On distilling off the ether, pure nitrosophenol remains.

Nitrosophenol crystallises, on slow evaporation of an ethereal solution, in large brown rhombic plates which have their brachydiagonal axis  $a$ , macrodiagonal  $b$ , and vertical axis  $c$  in the ratio  $a : b : c = 0.59264 : 1 : 2.4691$ ; and the angle  $\angle P = 118^\circ 41' 40''$ , and  $P : P = 120^\circ 5' 40''$ . It is moderately soluble in water, melts when heated, and at  $120^\circ$ – $130^\circ$  decomposes with a slight explosion. Nitrosophenol is readily soluble in a dilute solution of sodium hydrate; on adding a concentrated sodium hydrate solution, sodium-nitrosophenol separates in reddish-brown needles. On oxidation by nitric acid, or by an alkaline solution of potassium ferricyanide, it is converted into paranitrophenol (m. p.  $114^\circ$ ). By reduction with tin and hydrochloric acid it is converted into para-amidophenol. When nitrosophenol is dissolved in phenol, and a small quantity of concentrated sulphuric acid is added, the mass assumes a fine dark cherry-red colour, which changes to blue on the addition of water and solution of potassium hydrate. According to Liebermann (*ibid.* vii. 1099) the blue colouring matter thus produced has the composition  $\text{C}_{12}\text{H}_{10}\text{NO}$ , being formed by the action of 2 mols. of phenol on 1 mol. of nitrosophenol. To prepare it he mixes 5 grams of

phenol with an equal volume of concentrated sulphuric acid, carefully cooling to prevent, as far as possible, the formation of sulpho-acids; 20 grams of a 5 p.c. solution of potassium nitrite in concentrated sulphuric acid is then added in quantities sufficient to maintain the temperature at 40°–50° during the time that the reaction is taking place (about fifteen minutes). The liquid is then poured into a large quantity of cold water, the precipitate filtered off, drained on a porcelain plate, and dried over sulphuric acid. The substance thus obtained may be dried at 130°. It is a brown powder, easily soluble in alcohol; alkalis dissolve it, forming a blue solution.

The resin which is formed on acting upon phenol with dilute nitric acid is probably a product of the action of phenol on nitrosophenol (Baeyer a. Caro).

**Chloronitrophenols.** *Parachlorororthonitrophenol*,  $C^6H^4Cl(NO^2)OH$  (1 : 2 : 4), is the sole product of the action of dilute nitric acid on parachlorophenol (Faust, *Deut. Chem. Ges. Ber.* vi. 132; Beilstein a. Kurbatow, *ibid.* 1396); it is also formed, probably together with orthochlorororthonitrophenol, by the action of chlorine on orthonitrophenol (Faust a. Saame, *Ann. Ch. Pharm., Suppl.* vii. 195; Armstrong a. Prevost, *Deut. Chem. Ges. Ber.* vii. 922). It melts at 86°–87°. The properties and metallic derivatives of this phenol have already been described (1st *Suppl.* 912). It is converted by chlorine into dichlorororthonitrophenol melting at 121°–122°, and by nitric acid into Dubois' parachlorodinitrophenol melting at 81° (Faust a. Saame). The barium derivative crystallises with  $4H^2O$  and not with  $2H^2O$ , as previously stated (Faust, *Ann. Ch. Pharm.* clxxiii. 317).

*Orthochloroparanitrophenol*,  $C^6H^3Cl(NO^2)OH$  (1 : 2 : 4), is formed on chlorinating paranitrophenol (Armstrong, *Chem. Soc. J.* 1872, 12; Faust a. Müller, *Ann. Ch. Pharm.* clxxiii. 309); together with orthochlorororthonitrophenol, on treating orthochlorophenol (b. p. 176°) with dilute nitric acid (Faust a. Müller), and by Griess's method from the chloronitroamidophenol obtained on reducing chloro- $\alpha$ -dinitrophenol (m. p. 110°–111°) with ammonium sulphide (Faust, *Zeitschr. f. Chem.* 1871, 339).

Orthochloroparanitrophenol is slightly soluble in cold water and moderately soluble in boiling water, from which it separates partly as an oil which rapidly solidifies, partly in white silky needles; it is very soluble in ether, chloroform, and alcohol. It melts at 110°–111°, but at a much lower temperature under water. It is only volatile to a very slight extent in a current of steam. Nitric acid (sp. gr. 1.36) readily converts orthochloroparanitrophenol into chloro- $\alpha$ -dinitrophenol (m. p. 110°–111°); with chlorine it furnishes dichloroparanitrophenol (m. p. 125°). The *potassium derivative*,  $C^6H^3Cl(NO^2)OK + H^2O$ , forms tufts of brown-yellow needles very soluble in water; the *sodium derivative* forms yellow needles very soluble in water; the *calcium derivative*,  $(C^6H^3Cl(NO^2)O)^2Ca + 4H^2O$ , crystallises in tufts of canary-yellow needles, easily soluble in water; the *barium derivative*,  $(C^6H^3Cl(NO^2)O)^2Ba + 7H^2O$ , separates from hot water, in which it is very soluble, in long dark-yellow glistening needles; the *magnesium derivative* forms pale-yellow, very soluble needles, which contain a very large amount of water of crystallisation; the *silver derivative* crystallises from hot water in tufts of copper-brown, flattened needles, difficultly soluble in water.

*Orthochloroparamidophenol hydrochloride* is obtained on reducing orthochloroparanitrophenol with tin and hydrochloric acid. It crystallises from water, in which it is easily soluble, in white needles (Faust a. Müller).

*Orthochlorororthonitrophenol*,  $C^6H^4Cl(NO^2)OH$  (1 : 2 : 6), is formed, together with orthochloroparanitrophenol, when orthochlorophenol is added to nitric acid (sp. gr. 1.36) diluted with an equal weight of water (Faust a. Müller, *loc. cit.*). At first a red oil is produced, but after a time this becomes solid; it is allowed to remain for 24 hours in contact with the acid, then removed, washed, and boiled with barium carbonate. The difficultly soluble barium orthochlorororthonitrophenol is readily separated from the easily soluble barium orthochloroparanitrophenol by crystallisation.

Orthochlorororthonitrophenol is but slightly soluble in water; it dissolves easily in chloroform, from which it crystallises in flat yellow imperfectly developed needles. It volatilises readily in a current of steam, and may therefore be separated from orthochlorororthonitrophenol by distillation with water. It melts at 70°. Nitric acid converts it into chloro- $\alpha$ -dinitrophenol (m. p. 110°–111°). The *potassium derivative* crystallises in long dark-red glistening flat needles, easily soluble in water; the *calcium derivative*,  $(C^6H^3Cl(NO^2)O)^2Ca + H^2O$ , forms short red-brown prisms, which are often grouped in wart-like forms, and are somewhat difficultly soluble in water; the *barium derivative*,  $(C^6H^3Cl(NO^2)O)^2Ba + H^2O$ , forms short copper-brown plates, which are usually united in little warts; it is scarcely more soluble in hot than in cold water, very little separating from the hot saturated solution as it cools. The *silver derivative*,  $C^6H^3Cl(NO^2)OAg$ , forms carmine-red glistening scales, difficultly soluble in water.

*Dichloroparanitrophenol* or *Diorthochloroparanitrophenol*,  $C^6H^2Cl_2(NO^2)OH$  (1 : 2 : 4 : 6).—The preparation of this compound (m. p. 125°), which was first obtained by



Seifart by chlorination of paranitrophenol (m. p. 114°), has previously been described (1st Suppl. 913); in this case orthochloroparanitrophenol (m. p. 110°-111°) is first produced. It is also formed on carefully treating dichlorophenolsulphonic acid, prepared from phenolparasulphonic acid, with nitric acid (Armstrong, *Chem. Soc. J.* 1871, 1112; Faust, *Zeitschr. f. Chem.* 1871, 338). Seifart states that the barium derivative crystallises in brown-red prisms or light-red needles, according to concentration (1st Suppl. 913). According to Faust a. Müller, it forms either red flat needles with 4H<sup>2</sup>O or long yellow needles with 8H<sup>2</sup>O; the former separates first, the latter only appearing after some hours; both modifications yield both forms in the same order on recrystallisation (*Ann. Ch. Pharm.* clxxiii. 311). By the action of dilute nitric acid dichloroparanitrophenol may be converted into chloro- $\alpha$ -dinitrophenol (Armstrong, *loc. cit.*) When it is heated above its melting point it is decomposed with evolution of nitrogen, nitric oxide, and nitric peroxide; a sublimate consisting of long yellow needles of dichloroquinone and white prismatic crystals of an unknown body collects in the tube, and a brown-red residue is left (Armstrong a. Brown, *Deut. Chem. Ges. Ber.* vii. 926).

A dichloronitrophenol, described by Peterson as melting at 106° (*Ann. Ch. Pharm.* clviii. 163), has since been shown by him (*Deut. Chem. Ges. Ber.* 1873, 370) to be impure dichloroparanitrophenol.

*Dichlororthonitrophenol* or *Parachlorororthochlororthonitrophenol*, C<sup>6</sup>H<sup>2</sup>Cl<sup>2</sup>(NO<sup>2</sup>)OH (1 : 2 : 4 : 6), which is produced on nitrating the dichlorophenol melting at 42°-43° (1st Suppl. 913), is also formed when chlorine is passed into an aqueous solution of orthonitrophenolparasulphonic acid, and by the action of nitric acid on the dichlorophenolsulphonic acid produced by acting upon dichlorophenol (m. p. 42°-43°) with sulphuric chlorhydrate, which is doubtless identical with that formed on chlorinating Kekulé's phenolmetasulphonic acid (phenolorthosulphonic acid), (Armstrong, *Chem. Soc. J.* 1871, 1119; 1872, 93; Faust, *Zeitschr. f. Chem.* 1871, 338). The potassium derivative of this dichloronitrophenol, which is usually anhydrous, occasionally crystallises with a molecule of water (Faust, *Ann. Ch. Pharm.* clxxiii. 317).

*Dichlorororthamidophenol* or *Orthochloroparachlorororthamidophenol*, C<sup>6</sup>H<sup>2</sup>Cl<sup>2</sup>.NH<sup>2</sup>.OH (1 : 2 : 4 : 6).—The hydrochloride of this compound is readily obtained by reducing dichlororthonitrophenol (m. p. 121°) with tin and hydrochloric acid; when the action is completed it is precipitated by the addition of concentrated hydrochloric acid, redissolved in a small quantity of water, reprecipitated by acid, and dried on porous plates. It is readily converted into dichlorodiazophenol, C<sup>6</sup>H<sup>2</sup>Cl<sup>2</sup>ON<sup>2</sup>, which is obtained uncombined with hydrochloric acid, by the action of nitrous acid either on an aqueous or on an alcoholic solution (Schmitt a. Glutz, *Deut. Chem. Ges. Ber.* ii. 52).

*Orthochloro- $\alpha$ -dinitrophenol* or *Orthochlororthonitroparanitrophenol*, C<sup>6</sup>H<sup>2</sup>Cl(NO<sup>2</sup>)<sup>2</sup>OH (1 : 2 : 4 : 6).—This compound, which is the  $\beta$ -chlorodinitrophenol of Faust a. Saame, melting at 110°-111° (1st Suppl. 914), is identical with the chlorodinitrophenol ( $\gamma$ -chlorodinitrophenol; *ibid.*) obtained by Griess (Armstrong, *Chem. Soc. J.* 1872, 96), and with that formed on treating trinitrophenol according to Stenhouse's method (1st Suppl. 914) with iodine chloride (Peterson, *Deut. Chem. Ges. Ber.* vi. 368). It is also produced:—1. By the action of chlorine on  $\alpha$ -dinitrophenol (Armstrong, *Chem. Soc. J.* 1872, 12; Faust, *Zeitschr. f. Chem.* 1871, 339). 2. On nitration of orthochloroparanitrophenol (Armstrong, *loc. cit.*; Faust a. Müller, *Ann. Ch. Pharm.* clxxiii. 309). 3. On nitration of orthochlororthonitrophenol (Faust a. Müller). 4. By heating diazodinitrophenol from amidodinitrophenol (picramic acid) with hydrochloric acid (Faust, *loc. cit.*) 5. By the action of nitric acid on dichlorophenolparasulphonic acid (Armstrong, *Chem. Soc. J.* 1871, 119; Faust, *loc. cit.*) 6. By the action of nitric acid on dichloroparanitrophenol (Armstrong).

The potassium derivative, C<sup>6</sup>H<sup>2</sup>Cl(NO<sup>2</sup>)<sup>2</sup>OK + H<sup>2</sup>O, crystallises in short, fine, yellow needles; the sodium derivative, C<sup>6</sup>H<sup>2</sup>Cl(NO<sup>2</sup>)<sup>2</sup>ONa + 1½H<sup>2</sup>O, also in short yellow needles. The ammonium derivative crystallises with 1½OH<sup>2</sup>, and the barium derivative with 9-10OH<sup>2</sup>. *Calcium chloro- $\alpha$ -dinitrophenol*, [C<sup>6</sup>H<sup>2</sup>Cl(NO<sup>2</sup>)<sup>2</sup>O]<sup>2</sup>Ca + 7H<sup>2</sup>O, forms long, flat, pointed, golden-yellow needles; it is one of the most beautiful and characteristic of the derivatives of this phenol. The magnesium derivative crystallises in long, capillary, pointed, pale-yellow needles, which contain 7-10H<sup>2</sup>O according to concentration; the copper derivative, [C<sup>6</sup>H<sup>2</sup>Cl(NO<sup>2</sup>)<sup>2</sup>O]<sup>2</sup>Cu + 8H<sup>2</sup>O, forms long, hair-fine, branched, silky needles of greenish-yellow colour, which become dark brown on drying. All these are readily soluble in hot water, but difficultly soluble in cold water.

*Orthochlorororthamidoparanitrophenol*, C<sup>6</sup>H<sup>2</sup>Cl(NH<sup>2</sup>)(NO<sup>2</sup>)OH (1 : 2 : 4 : 6), is obtained on reducing chloro- $\alpha$ -dinitrophenol by ammonium sulphide (Faust, *Zeitschrift f. Chem.* 1871, 339; *Ann. Ch. Pharm.* clxxiii. 316; Armstrong, *Chem. Soc. J.* 1872, 14). It separates from hot water, in which it is moderately soluble, in long, fine, brass-yellow needles.

needles of the composition,  $C^6H^3Cl(NH^2)NO^2OH + \frac{1}{2}H^2O$ . The dry substance melts at about  $140^\circ$ . The *barium derivative*,  $[C^6H^3Cl(NH^2)(NO^2O)]^2Ba + 4H^2O$ , crystallises in fine, black needles; the *sulphate*,  $[C^6H^3Cl(NH^2)(NO^2O)]^2H^2SO^4$ , separates from the saturated solution in yellowish, glistening plates, rather soluble in water; the *hydrochloride*,  $C^6H^3ClNH^2NO^2OH.HCl$ , crystallises in short, yellow needles, and is easily soluble in water.

*Parachloro- $\beta$ -dinitrophenol* or *Parachlorodiorthonitrophenol*,  $C^6H^2Cl(NO^2)^2OH$  (1 : 2 : 4 : 6). This modification, which melts at  $80^\circ$ – $81^\circ$ , is commonly known as Dubois chlorodinitrophenol. It is produced:—1. By nitration of parachlorophenol (Dubois). 2. By the action of nitric acid on parachlorophenolsulphonic acid (Petersen a. Baehr-Predari, *Ann. Ch. Pharm.* clvii. 156). 3. On nitration of parachlororthonitrophenol melting at  $86^\circ$ – $87^\circ$  (Faust a. Suame). 4. By the action of sodium hydrate solution on the  $\alpha$ -dinitroparadiachlorobenzene (m. p.  $104^\circ$ ) of Jungfleisch (Engelhardt a. Latschinoff, *Zeitschr. f. Chem.* 1870, 234; Körner, *Gaz. chim. ital.* 1874, 395). 5. On chlorination of  $\beta$ -dinitrophenol (Armstrong, *Deut. Chem. Ges. Ber.* 1873, 649; Körner *loc. cit.*) 6. In small quantity together with chloro- $\alpha$ -dinitrophenol by the action of iodine chloride on trinitrophenol (Petersen, *Deut. Chem. Ges. Ber.* 1873, 369; Armstrong, *ibid.* 650).

Parachloro- $\beta$ -dinitrophenol crystallises in monoclinic prisms which exhibit the combinations OP.—P. +  $P\infty$ .  $\infty P\infty$ ; the cleavage being according to  $\infty P\infty$ . The orthodiagonal axis (a), the klinodiagonal (b), and the principal axis (c) are in the ratio  $a : b : c = 0.59553 : 1 : 0.73070$ , and the angles  $\infty P : \infty P = 64^\circ 34'$ ;  $OP : P\infty = 137^\circ 40'$ ;  $OP : \infty P\infty = 109^\circ 30'$ ;  $OP : \infty P = 100^\circ 17'$ ;  $OP : -P = 132^\circ 0'$  (Hessenberg, *Ann. Ch. Pharm.* clvii. 158).

The *potassium derivative*,  $C^6H^2Cl(NO^2)^2OK$ , crystallises in long, fine needles of a magnificent red colour, which exhibit a metallic-green lustre; it is readily soluble in hot, but very difficultly soluble in cold water. The *ammonium derivative*,  $C^6H^2Cl(NO^2)^2ONH^4$ , forms fine, deep orange needles; the *sodium derivative*,  $C^6H^2Cl(NO^2)^2ONa + 3H^2O$ , separates in scarlet-red moss-like forms, difficultly soluble in cold water; from alcohol it crystallises in small red needles. The *barium derivative*,  $[C^6H^2Cl(NO^2)^2O]^2Ba + H^2O$ , crystallises in fine, glistening, pale saffron-yellow needles, very difficultly soluble even in hot water; the *lead derivative*,  $[C^6H^2Cl(NO^2)^2O]^2Pb + H^2O$ , is also very difficultly soluble in hot water, from which it separates in fine, glistening, yellow needles. The *copper derivative*,  $[C^6H^2Cl(NO^2)^2O]^2Cu + 2H^2O$ , forms saffron-yellow needles. The *silver derivative*,  $C^6H^2Cl(NO^2)^2OAg$ , which is very difficultly soluble in water, separates from the hot solution in fine, brilliant-red needles.

*Parachloro- $\beta$ -dinitrophenol*,  $C^6H^2Cl(NO^2)^2OC^2H^3$ , crystallises from alcohol in almost colourless, glistening needles, or pale yellow rhombic plates. It melts at  $54^\circ$ – $55^\circ$  (Petersen a. Baehr-Predari).

*Other Chlorodinitrophenols*.—By heating *s*-dinitroparadiachlorobenzene (m. p.  $101^\circ$ ) with sodium hydrate solution, Engelhardt a. Latschinoff (*Zeit. f. Chem.* 1870, 234) obtained the sodium derivative of a *dinitroparachlorophenol* melting at  $70^\circ$ , isomeric with parachloro- $\beta$ -dinitrophenol. This observation has recently been confirmed by Körner (*Gaz. chim. ital.* 1874, 395). According to the latter, the potassium derivative of this phenol crystallises in small plates of the same colour as the silver derivative of Dubois' chlorodinitrophenol.

A *metachlorodinitrophenol* has been obtained by Körner (*loc. cit.* 375, 400) by treating the dinitrometadiachlorobenzene (m. p.  $103^\circ$ ), formed on nitrating metadiachlorobenzene (1 : 3) with potassium hydrate. The potassium derivative which is thus produced is yellow, and only slightly soluble in water.

Petersen a. Baehr-Predari (*Ann. Ch. Pharm.* clvii. 161) obtained a small quantity of a *dinitrochlorophenol*, melting at  $114^\circ$ , together with Dubois' chlorodinitrophenol, on nitrating the sulpho-acid from chlorophenol (b. p.  $218^\circ$ ). Whether, if a pure substance, this was derived from the parachlorophenol, or, which appears to be more probable, from metachlorophenol present in the parachlorophenol employed, was not determined. The metallic derivatives of this compound are more soluble than, and not so well crystallised as, those of parachloro- $\beta$ -dinitrophenol. The *potassium derivative*,  $C^6H^2Cl(NO^2)^2OK + H^2O$ , crystallises in brick-red, moss-like aggregates; when dry it has a brilliant carmine-red colour. The *ammonium derivative*,  $C^6H^2Cl(NO^2)^2ONH^4 + H^2O$ , forms orange-yellow needles; the *barium derivative*,  $[C^6H^2Cl(NO^2)^2O]^2Ba + 2H^2O$ , crystallises in ochre-yellow needles, which become orange-red on drying; the *silver derivative* separates from hot water in small, granular, pale-red crystals.

The *dinitrochlorophenol* melting at  $69^\circ$  which Petersen (*loc. cit.* 165) described as isomeric with Dubois' chlorodinitrophenol, he has since stated (*Deut. Chem. Ges. Ber.* vi. 369) is identical with the latter.

**Bromonitrophenols.** *Parabromonitrophenol*,  $C^6H^4Br(NO^2)OH$  (1 : 2 : 4), is the first product of the action of nitric acid on parabromophenol (Huebner a. Brenken, *Deut. Chem. Ges. Ber.* vi. 170; Körner, *Gaz. chim. ital.*, 1874, 388; Armstrong). It melts at 87°–88°. The sodium derivative,  $C^6H^4Br(NO^2)ONa$ , crystallises in small deep-red needles, which exhibit a golden-green lustre, it is extremely soluble in water.

*Orthobromoparanitrophenol*,  $C^6H^4Br(NO^2)OH$  (1 : 2 : 4), is produced when bromine acts upon paranitrophenol. It melts at 102° (1st Suppl. 912). The barium derivative,  $[C^6H^4Br(NO^2)O]^2Ba + 6H^2O$ , crystallises in tufts of orange-yellow needles, somewhat difficultly soluble in water (Brunck, *Zeitschr. f. Chem.* 1867, 204).

*Orthobromonitrophenol*,  $C^6H^4Br(NO^2)OH$  (1 : 2 : 6), is apparently formed, together with parabromonitrophenol, by the action of bromine on orthonitrophenol (Armstrong a. Prevost, *Deut. Chem. Ges. Ber.* vii. 922), but it has not yet been separated in the pure state.

*Dibromoparanitrophenol* or *Diorthobromoparanitrophenol*,  $C^6H^2Br^2(NO^2)OH$  (1 : 2 : 4 : 6), which is the end-product of the action of bromine on paranitrophenol (1st Suppl. 912), is also formed by nitration of dibromophenolparasulphonic acid (Armstrong a. Brown, *Chem. Soc. J.* 1872, 857). When heated slightly above its melting point (141°), it is decomposed; nitrogen, nitric oxide, and nitric peroxide are evolved, and a sublimate of dibromoquinone mixed with a second body is obtained in the tube in which the decomposition is effected, and a brown residue remains (Armstrong).

*Dibromoparanitranisol*,  $C^6H^2Br^2(NO^2)OCH^3$ , crystallises in white prisms melting at 122·6°; it is slightly soluble in cold alcohol, but more soluble in hot alcohol. When digested with alcoholic ammonia at 180°, it is converted into dibromoparanitroaniline, melting at 202·5°, which, on treatment with ethyl nitrite, furnishes nitrometadibromobenzene, melting at 104·5° (Körner, *Gaz. chim. ital.*, 1874, 390).

*Dibromonitrophenol* or *Parabromonitrophenol*,  $C^6H^4Br^2(NO^2)OH$  (1 : 2 : 4 : 6).—This is formed by the action of bromine in excess on orthonitrophenol. It is also produced by nitration of ordinary dibromophenol (1st Suppl. 912), by nitration of dibromophenolorthosulphonic acid (Armstrong a. Brown, *loc. cit.* 863), and by the action of bromine on orthonitrophenolparasulphonic acid (*ibid.* 870). It melts at 117°–118°. The voluminous brown-red precipitate of the silver derivative which forms on adding silver nitrate to a dilute boiling solution of the potassium derivative, is converted, on standing 24 hours, into red needles 5–6 mm. long, which exhibit a brilliant metallic lustre; in the dry state these crystals resemble rapidly crystallised potassium chrysammate (Körner).

*Dibromonitranisol*,  $C^6H^2Br^2(NO^2)OCH^3$ , which is produced on digesting the silver derivative with methyl iodide, crystallises in long needles which exhibit a slight yellowish-green tinge; it melts at 76·7°. It is converted by alcoholic ammonia at 170° into dibromonitroaniline (m. p. 127·3°), which, on treatment with ethyl nitrite, furnishes the same nitrometadibromobenzene (m. p. 104·5°) that is obtained from dibromoparanitrophenol by a similar series of reactions (Körner, *loc. cit.* 392).

*Orthobromo- $\alpha$ -dinitrophenol* or *Orthobromonitroparanitrophenol*,  $C^6H^4Br(NO^2)_2OH$  (1 : 2 : 4 : 6), was first obtained by Laurent (*Rev. Scient.* vi. 65) by the action of bromine on  $\alpha$ -dinitrophenol. It is also produced: 1. On nitration of orthobromoparanitrophenol (Körner, *loc. cit.* 394; Armstrong). 2. On nitration of orthobromophenol (Körner; Armstrong). 3. Together with parabromo- $\beta$ -dinitrophenol on nitrating the product of the action of 1 mol. of bromine on orthonitrophenol, being formed doubtless from the orthobromonitrophenol present in the mixture (Armstrong a. Prevost). 4. On nitration of dibromophenolparasulphonic acid (Armstrong a. Brown, *Chem. Soc. J.* 1872, 861). 5. On nitration of bromophenoldisulphonic acid (Armstrong, *ibid.* 865). 6. By digesting trinitrophenol with bromine iodide and water (Armstrong, *Deut. Chem. Ges. Ber.* vi. 650). 7. By the action of potassium hydrate solution on the bromodinitroaniline (m. p. 144°) obtained on treating ordinary dinitroaniline (1 : 2 : 4) with bromine (Körner, *loc. cit.* 394).

*Orthobromo- $\alpha$ -dinitrophenol* melts at 118·2° (Körner). It separates from boiling water, in which, however, it is only slightly soluble, in short, fine, almost colourless needles. It is readily soluble in hot alcohol, from which it crystallises in long hair-fine needles. The potassium derivative,  $C^6H^4Br(NO^2)_2OK + H^2O$ , forms brilliant yellow flat needles; it also separates in orange prismatic needles containing 1 mol. of water, and the salt with  $1\frac{1}{2}$  mol. of water readily parts with the  $\frac{1}{2}$  mol. on exposure to the air. Both forms are difficultly soluble in cold water, although readily dissolved by hot water. The barium derivative,  $[C^6H^4Br(NO^2)_2O]^2Ba + 4-6H^2O$ , is very difficultly soluble in water; it crystallises in short needles of a more or less deep yellow colour, according to the state of concentration and temperature of the solution from which it separates; the darker forms always contain more water of crystallisation.

tion than the lighter. The calcium derivative,  $[\text{C}^6\text{H}^3\text{Br}(\text{NO}^2)_2\text{O}]^+\text{Ca} + 7 - 8\text{H}_2\text{O}$ , is readily soluble in hot water, but difficultly in cold; it separates from a hot concentrated solution in brilliant orange-red rhombic plates, and from very dilute solutions in short fine yellow needles (Armstrong a. Brown). According to Huebner a. Brecken the yellow salt contains  $12\text{OH}^2$ . The orange-red form is gradually converted into the yellow if it be allowed to remain in the solution.

The bromodinitroaniline (m. p.  $144^\circ$ ) from which this bromodinitrophenol may be obtained (*supra*) is not attacked by ethyl nitrite (Körner).

**Parabromo- $\beta$ -dinitrophenol** or **Parabromodithionitrophenol**,  $\text{C}^6\text{H}^3\text{Br}(\text{NO}^2)_2\text{OH}$  (1 : 2 : 4 : 6).—This compound, first obtained by Körner on nitration of crude bromophenol (*Ann. Ch. Pharm.* cxxxvii. 205), is formed: 1. By the action of nitric acid on parabromophenol (Körner, *Gaz. chim. ital.*, 1874, 388; Armstrong). 2. By the action of nitric acid on pure parabromorthonitrophenol (Armstrong), so that it is produced, together with orthobromo- $\alpha$ -dinitrophenol, on nitrating the mixture of parabrom- and orthobrom-orthonitrophenol formed by the action of 1 mol. of bromine on orthonitrophenol (Armstrong a. Prevost, *Deut. Chem. Ges. Ber.* vii. 922). 3. By the action of bromine on  $\beta$ -dinitrophenol (Körner, *loc. cit.* 327, 397; Armstrong). It is very difficultly soluble even in boiling water, and separates on cooling in short yellow needles. From ether, in which it dissolves easily, it crystallises in large orange prisms. It melts at  $75.6^\circ$  (Körner). When heated with water and bromine on the water-bath, bromo- $\beta$ -dinitrophenol is converted into bromo- $\alpha$ -dinitrophenol; hence it is necessary, in the preparation of bromo- $\beta$ -dinitrophenol from  $\beta$ -dinitrophenol and bromine, to warm the mixture gently to  $50^\circ$ – $60^\circ$  (Armstrong). The potassium derivative,  $\text{C}^6\text{H}^3\text{Br}(\text{NO}^2)_2\text{OK}$ , which is very difficultly soluble in cold water, and far less soluble in boiling water than potassium orthobromo- $\alpha$ -dinitrophenol, crystallises in magnificent flat crimson needles, which exhibit a beautiful metallic-green lustre, especially when viewed surrounded by water. The silver derivative resembles most closely that of the corresponding (Dubois') chlorodinitrophenol, but has a slightly deeper colour.

**Other Bromodinitrophenols.** **Metabromodinitrophenol**,  $\text{C}^6\text{H}^3\text{Br}(\text{NO}^2)_2\text{OH}$ .—The potassium derivative of this compound is obtained on heating the dinitrometadibromobenzene (m. p.  $117.4^\circ$ ), which is produced by the action of a mixture of nitric and sulphuric acids on nitrometadibromobenzene (1 : 3 : 4) melting at  $61.6^\circ$ , with an aqueous solution of 2 mols. of potassium hydrate. It is also formed on nitration of metabromophenol (1 : 3; Körner, *loc. cit.* 389, 398). It is easily soluble in alcohol and ether, from which it crystallises in large transparent, almost colourless prisms; it is precipitated from a concentrated cold aqueous solution by hydrochloric acid in small plates, and from a hot, less concentrated, solution in long needles. It is soluble in concentrated nitric acid, but precipitated in plates on the addition of water. It melts at  $91.5^\circ$ . The potassium derivative is dimorphous. If crystallised from the nearly boiling solution, it separates in long bright yellow anhydrous needles, which present a magnificent setaceous appearance; and these, if left in the solution, suddenly assume a paler colour; also if the darker salt be heated to  $120^\circ$  the crystals fall to a powder consisting of minute crystals of the lighter salt. When crystallised at a very low temperature, the potassium derivative forms large transparent bright-yellow rhombic plates which contain water of crystallisation; these very readily part with their water, even when immersed in the solution, and become opaque. The calcium and barium derivatives are obtained on the addition of calcium or barium chloride to a hot solution of the potassium derivative, in long yellow pointed needles. They detonate more violently than potassium trinitrophenol when heated. The silver derivative is thrown down as a bulky yellow precipitate on the addition of silver nitrate to a solution of the potassium derivative; when touched with a glass rod it assumes a magnificent red colour at the point of contact, which soon extends to the whole mass. When it is dissolved in a large quantity of boiling water, and the solution is cooled, it separates in small needles and laminae, perfectly united in strawberry-like forms, of a magnificent dark crimson-red colour, which rival velvet in softness and splendour. **Metabromodinitranisole**,  $\text{C}^6\text{H}^3\text{Br}(\text{NO}^2)_2\text{OCH}^3$ , crystallises from ether in small prisms, from alcohol in rhombic plates of a greenish-yellow colour; it melts at  $109.4^\circ$  (Körner).

**Iodonitrophenols.** **Orthiodoparanitrophenol**,  $\text{C}^6\text{H}^3\text{I}(\text{NO}^2)_2\text{OH}$  (1 : 2 : 4), which melts at  $93^\circ$ – $94^\circ$ , has already been described (1st Suppl. 914). Busch's statement (*Deut. Chem. Ges. Ber.* vii. 462) that the iodonitrophenol obtained by the action of iodine and mercuric oxide on non-volatile nitrophenol does not possess the properties ascribed to it by Körner, and that it melts at  $154^\circ$ – $155^\circ$ , is incorrect; the substance he obtained was undoubtedly diiodoparanitrophenol (Armstrong). Orthiodoparanitrophenol is readily converted into iodo- $\alpha$ -dinitrophenol (m. p.  $106^\circ$ ) by the action of nitric acid (Armstrong).

**Iodorthonitrophenols**,  $C^6H^4I(NO^2)OH$ .—According to Busch the action of iodine and mercuric oxide on orthiodonitrophenol (volatile nitrophenol) dissolved in glacial acetic acid, gives rise to the formation of two isomeric iodonitrophenols, viz:  $\alpha$ -iodonitrophenol, which melts at  $90^\circ$ – $91^\circ$ , crystallising in long yellow needles, easily soluble in hot water, alcohol, and ether; and  $\beta$ -iodonitrophenol, which melts at  $66^\circ$ – $67^\circ$ , and crystallises in short yellow needles easily soluble in hot water, alcohol, and ether. The  $\alpha$ -compound is difficultly volatile in a current of steam; the  $\beta$ -compound, however, volatilises readily. Potassium- $\alpha$ -iodonitrophenol,  $C^6H^3I(NO^2)OK$ , forms red needles very easily soluble in water, but difficultly soluble in alcohol; the  $\beta$ -derivative,  $C^6H^3I(NO^2)OK + H^2O$ , crystallises in small golden-red glistening plates, very easily soluble in water and alcohol. Busch's description of the iodonitrophenols from orthonitrophenol appears to be very incorrect (Armstrong). When the product of the action of iodine and mercuric oxide is submitted to distillation in a current of steam, orthonitrophenol, together with a certain quantity of iodorthonitrophenol, passes over; the residue consists of iodo- and diiodo-orthonitrophenol. If the volatilised portion be dissolved in potassium carbonate solution, the potassium derivative of an iodonitrophenol separates in crystals, such as, according to Busch, are formed by potassium  $\beta$ -iodonitrophenol; but the phenol from these, after repeated recrystallisation from alcohol, melts at  $109^\circ$ – $110^\circ$ , and furnishes a potassium derivative,  $C^6H^3I(NO^2)OK + H^2O$ , crystallising in aggregates of somewhat irregularly developed rhombic plates of a magnificent garnet-red colour by transmitted light; in reflected light these crystals exhibit a beautiful golden-green metallic lustre; they are easily soluble in hot, but difficultly soluble in cold water and alcohol. When the mixture of iodo- and diiodonitrophenol above referred to is treated with potassium carbonate solution, the solution evaporated to dryness, and the mixture of dry salts extracted with boiling alcohol, a considerable quantity of the potassium derivative of the phenol melting at  $109^\circ$ – $110^\circ$  is likewise obtained; this iodorthonitrophenol crystallises in orange prisms or needles; it is readily soluble in boiling alcohol, but difficultly soluble in cold alcohol; it is only very slightly soluble in water, and does not volatilise to any considerable extent in a current of steam. Busch's  $\alpha$ -iodonitrophenol was probably impure diiodonitrophenol (m. p.  $98^\circ$ ).

**Orthiodo- $\alpha$ -dinitrophenol** or **Orthiodorthonitrophenol**,  $C^6H^3I(NO^2)_2OH$  (1 : 2 : 4 : 6).—This compound was first obtained, but in an impure state, by the action of iodine and iodic acid on  $\alpha$ -dinitrophenol by Körner. It is also produced: 1. By the action of iodine and mercuric oxide on  $\alpha$ -dinitrophenol (Armstrong, *Deut. Chem. Ges. Ber.* vi. 651; Weselsky, *Ann. Ch. Pharm.* clxxiv. 111). 2. By the action of hydriodic acid on diazodinitrophenol (Körner; Armstrong). 3. By the action of nitric acid on orthiodoparanitrophenol (Armstrong). It crystallises from boiling water, in which, however, it is only sparingly soluble, in long fine lemon-yellow needles which melt at  $106^\circ$  (Armstrong),  $108^\circ$  (Weselsky). The potassium derivative,  $C^6H^2I(NO^2)_2OK$ , forms deep orange coloured needles, easily soluble in hot, but difficultly in cold water. The calcium derivative,  $[C^6H^2I(NO^2)_2O]Ca + 5H^2O$ , crystallises in beautiful orange-red monoclinic (?) plates, easily soluble in hot water, but difficultly in cold; the barium derivative crystallises in flat needles of the colour of potassium dichromate.

**Paraiodo- $\beta$ -dinitrophenol** or **Paraiododionitrophenol**,  $C^6H^3I(NO^2)_2OH$  (1 : 2 : 4 : 6), is produced by the action of iodine and mercuric oxide on an alcoholic solution of  $\beta$ -dinitrophenol (Armstrong, *Deut. Chem. Ges. Ber.* vi. 649). The potassium derivative is obtained when iodine and iodic acid are added to a solution of  $\beta$ -dinitrophenol in a large excess of potassium hydrate solution, and the liquid alternately rendered acid and alkaline (Körner, *Gaz. chim. ital.*, 1874, 397). It crystallises from water, in which it is very sparingly soluble, in short fine yellow needles, melting at  $113^\circ$ . The potassium derivative forms magnificent carmine-red needles, which, however, when viewed in certain directions, exhibit the splendid metallic-green appearance of mercuric oxide, and in others a golden-yellow colour; it is very difficultly soluble in water. The silver derivative is precipitated by silver nitrate from a dilute boiling solution of the potassium derivative in magnificent brown-red small needles.

**Sulpho-phenols or Phenolsulphonic Acids.** The experiments of Faust (*Zeitschr. f. Chem.* 1871, 339), of Armstrong, and of Armstrong & Brown (*Chem. Soc. J.* 1871, 1112; 1872, 12, 857), do not lend support to Solomonoff's statement (1st Suppl. 924) that the action of sulphuric acid on phenol produces simultaneously three isomeric phenolmonosulphonic acids,  $C^6H^4.OH.SO^2H$ , but confirm Kekulé's view that only two are formed.

**Phenolorithosulphonic acid.** Kekulé's Phenolmetasulphonic acid ( $\beta$ -Phenylsulphuric acid; 1st Suppl. 923).  $C^6H^3.OH.SO^2H$  (1 : 2). Solomonoff's experiments (*Zeitschr. f. Chem.* 1869, v. 296) on the action of benzoyl

chloride on potassium phenolorthosulphonate do not in the least confirm Engelhardt a. Latschinoff's view that the  $\alpha$ - and  $\beta$ -acids formed from phenol and sulphuric acid are related in the same manner as isethionic acid and hydrogen ethyl-sulphate, but are quite in accordance with the view that both are oxybenzenesulphonic acids, since by heating the potassium salt of the  $\beta$ -acid with benzoyl chloride, he obtained *benzophenid*,  $\text{C}^6\text{H}_4(\text{OH})\cdot\text{CO}\cdot\text{C}^6\text{H}_5$ , and not benzophenone,  $\text{C}^6\text{H}_5\cdot\text{CO}\cdot\text{C}^6\text{H}_5$  (1st Suppl. 926); the precise nature of the reaction which takes place cannot, however, be stated, as the composition of the product containing sulphur has not been ascertained.

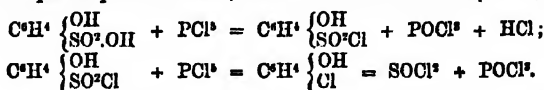
When heated with water and hydrochloric or sulphuric acid in sealed tubes at about  $140^\circ$ , phenolorthosulphonic acid yields phenol and sulphuric acid (Armstrong).

Aniline-phenolorthosulphonate,  $\text{C}^6\text{H}_4(\text{OH})\cdot\text{SO}^2(\text{NH}^+\text{C}^6\text{H}_5)$ , is resolved into phenol and sulphanilic acid when carefully distilled (Kopp, *Deut. Chem. Ges. Ber.* iv. 978):  $\text{C}^6\text{H}_4(\text{OH})\cdot\text{SO}^2(\text{NH}^+\text{C}^6\text{H}_5) = \text{C}^6\text{H}_5\cdot\text{OH} + \text{C}^6\text{H}_5\cdot\text{NH}^+\cdot\text{SO}^2\text{H}$ . By the action of nitric acid on potassium phenolorthosulphonate, the potassium salt of a nitrophenolorthosulphonic acid is produced, which does not appear to be identical with that formed from paranitrophenol and sulphuric acid (Post, *ibid.* vii. 1323).

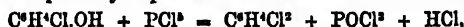
*Phenolparasulphonic acid*,  $\text{C}^6\text{H}_4\cdot\text{OH}\cdot\text{SO}^2\text{H}$  (1 : 4).—According to Kekulé, potassium phenolparasulphonate yields resorcin when fused with an excess of potassium hydrate, although always in small quantity. Lincke (*J. pr. Chem.* [2], viii. 43) has made a series of experiments on this subject, and also finds that very little resorcin is produced, but at temperatures above  $300^\circ$  a reaction occurs which results in the formation of a diphenol,  $\text{C}^{12}\text{H}_8(\text{OH})^2$ , isomeric with that obtained by Barth on fusing phenol with potassium hydrate, but identical with the diphenol which Griess procured by heating tetrazodiphenyl nitrate with water (iv. 412).

Aniline-phenolparasulphonate melts at about  $170^\circ$  and decomposes at  $180^\circ$ – $190^\circ$ , pure phenol distilling over, and a residue of sulphanilic acid being left (Kopp). Phenolparasulphonic acid is decomposed into phenol and sulphuric acid on heating with water and sulphuric or hydrochloric acid in sealed tubes at about  $150^\circ$ ; it is, however, far less readily decomposed than the isomeric acid (Armstrong).

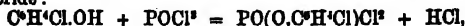
When potassium phenolparasulphonate is heated for some time with double the weight of phosphorus pentachloride in a flask or retort connected with a reversed condenser, and then distilled, a product is obtained which, on rectification, yields a mixture of sulphurous chloride,  $\text{SOCl}_2$ , and phosphoric chloride,  $\text{POCl}_3$ , boiling at  $60^\circ$ – $120^\circ$ ; from the higher portions of the distillate an oil boiling at  $265^\circ$ – $267^\circ$  may be separated by rectification, and, when the intermediate portions are added to water, a considerable quantity of paradi-chlorobenzene is obtained, together with a solution containing hydrochloric, phosphoric, and monochlorophenolphosphoric acids. The dichlorobenzene boils at  $173^\circ$ – $174^\circ$ , and melts at  $53^\circ$ – $54^\circ$ . The oil boiling at about  $265^\circ$  has the composition  $\text{C}^6\text{H}^4\text{Cl}^2\text{PO}^2 = \text{POCl}_2(\text{OC}^6\text{H}^4\text{Cl})$ ; it is converted by water into chlorophenylphosphoric acid,  $\text{PO}(\text{OH})^2(\text{OC}^6\text{H}^4\text{Cl})$ , and by heating with phosphorus pentachloride into dichlorobenzene. When heated with water in sealed tubes, chlorophenylphosphoric acid is readily converted into parachlorophenol (b. p.  $217^\circ$ ) and phosphoric acid. The first action of the pentachloride appears to consist in the formation of phenolparasulphonic chloride, which then furnishes chlorophenol; thus:



The chlorophenol is probably in part at once converted into dichlorobenzene:



but is mainly converted by the action of the phosphoric chloride into chlorophenylphosphoric chloride:



which doubtless in part also undergoes conversion into dichlorobenzene (Barbaglia a. Kekulé, *Deut. Chem. Ges. Ber.* v. 875; vi. 943).

*Phenoldisulphonic acid*. *Phenolorthoparadisulphonic acid*,  $\text{C}^6\text{H}_3\cdot\text{OH}\cdot(\text{SO}^2\text{H})^2$  (1 : 2 : 4).—This compound (1st Suppl. 926) is produced when diazobenzenesulphonic acid from sulphanilic acid is warmed with fuming sulphuric acid (Armstrong a. Prevost, *Deut. Chem. Ges. Ber.* vi. 664).

*Phenoltrisulphonic acid*,  $\text{C}^6\text{H}_2\cdot\text{OH}\cdot(\text{SO}^2\text{H})^3$  (Senhofer, *Ann. Ch. Pharm.* clix. 110; Annenheim, *ibid.* clix. 28).—To prepare this acid, 16 grams of phosphoric anhydride and 30 grams of concentrated sulphuric acid are introduced into a strong glass tube and mixed to a thin paste with the aid of a glass rod; 6 grams of phenol is then added, care being taken to mix the liquids as little as possible; the tube sealed;

the contents carefully mixed; and the tube heated for several hours at 180°. The product is boiled with a large quantity of water until the smell of sulphurous anhydride is no longer apparent, an excess of milk of lime is added, and the precipitate separated by filtration; the residue is once or twice boiled with water, and the liquid added to the first filtrate. The filtrate is then treated, first with hydrogen-potassium carbonate, in order to remove the dissolved calcium hydrate, and afterwards with dipotassium carbonate until the whole of the calcium is precipitated as carbonate; a solution containing basic and normal potassium phenoltrisulphonate is thus obtained, from which the former is separated by crystallisation. When, on further evaporation, a pasty mass only is obtained, the whole is acidulated with acetic acid and evaporated to dryness; the potassium acetate is then extracted by alcohol; and the residue of tripotassium phenoltrisulphonate purified by several recrystallisations from water. To obtain the free acid, a solution of either of the potassium salts is precipitated with basic lead acetate, the precipitate is suspended in water at 100°, and decomposed by hydrogen sulphide; and the filtrate from the lead sulphide is evaporated on the water-bath to a syrup, from which the acid separates in fine needles (Senhofer). Annenheim obtained phenoltrisulphonic acid by heating oxybenzenesulphone (oxysulphobenzide),  $(C^6H^4.OH)SO_2$ , with thrice its weight of fuming sulphuric acid, at 180°-190° for 1 to 2 hours.

Phenoltrisulphonic acid crystallises in stellate groups of needles or in short thick prisms, containing water of crystallisation; it is extremely hygroscopic, and rapidly deliquesces on exposure to the air. The crystals dried at 100° contain  $3\frac{1}{2}$  mols. of water. It begins to decompose, with separation of sulphuric acid, on heating at 105°. It is not affected by boiling with nitric acid, but is decomposed by bromine-water. A solution of the free acid, or of one of its soluble salts, is coloured a deep blood-red by ferric chloride. *Barium phenoltrisulphonate*,  $[C^6H^4.OH.(SO_3H)]_2Ba + 4H_2O$ , forms white crystalline scales, which dissolve in water with difficulty (Senhofer). Annenheim obtained a salt with 10 mols. of water, crystallising in small glistening prismatic plates. *Tripotassium phenoltrisulphonate*,  $C^6H^4.OH.(SO_3K)_3 + 4H_2O$ , crystallises in rhombic plates, easily soluble in water; the *tetrapotassium salt*,  $C^6H^4.OK.(SO_3K)_4 + 2H_2O$ , forms long flat concentrically grouped needles. The *silver salt*,  $(C^6H^4.OH.(SO_3Ag))_2 + 1\frac{1}{2}H_2O$ , crystallises in fine needles. The *basic lead salt*,  $(C^6H^4SO_3O^1Pb)_2 \cdot 2PbH^2O + 4\frac{1}{2}H_2O$ , is obtained as a heavy white crystalline powder, almost insoluble in water, on the addition of basic lead acetate to a solution of either of the potassium salts. *Sodium phenoltrisulphonate*,  $C^6H^4SO_3O^1Na + 3H_2O$ , forms very soluble colourless needles. *Cadmium phenoltrisulphonate*,  $C^6H^4SO_3O^1Cd + 7H_2O$ , crystallises in flat plates; the *copper salt* forms long fine green needles, which are very soluble; the *ammonium salt* forms crystalline scales, very soluble in water.

*Phenoltetrasulphonic acid*,  $C^6H.OH.(SO_3H)_4$ .—Annenheim (*loc. cit.*) obtained a potassium salt crystallising in small rhombic prisms, of the composition of potassium phenoltetrasulphonate, from the product of the action of 500 grams of fuming sulphuric acid on 125 grams of phenol at 190°-200°.

**Chlorophenolsulphonic acids.**—*a-Parachlorophenolsulphonic acid* or *Parachlorophenolorthosulphonic acid*,  $C^6H^3Cl.OH.SO_3H$  (1 : 2 : 4), is prepared by heating a mixture of parachlorophenol (1 : 4) with the equivalent quantity of fuming sulphuric acid for several hours on the water-bath, &c. (Peterson a. Baehr-Predari, *Ann. Ch. Pharm.* clvii. 121; 1st Suppl. 924). It crystallises from the concentrated aqueous solution in large, colourless, glistening plates, containing 1 mol. of water; the pure acid melts at 75°-76°, and begins to decompose at about 100°. The acid and all its salts yield an intense blue-violet colour with ferric chloride. On fusing the potassium salt with an excess of potassium hydrate at 160°, a small quantity of pyrogallol, together with traces of hydroquinone, is obtained. Nitric acid readily converts the acid and its salts into parachloro-*B*-dinitrophenol, melting at 81° (Peterson a. Baehr-Predari); the formation of this compound is preceded by that of a nitrochlorosulphonic acid (Armstrong, *Deut. Chem. Ges. Ber.* vii. 404). *Potassium chlorophenolsulphonate*,  $C^6H^3Cl.OH.SO_3K + 2H_2O$ , forms flat, monoclinic prisms; the anhydrous salt dissolves at 20° in 9.25 pts. of water, and at 100° in 2.24 pts. On recrystallising this salt from strong alcohol, glistening quadratic plates containing 1 mol. of water are obtained; an anhydrous salt, crystallising in small needles, is obtained if absolute alcohol be employed. The *sodium salt*,  $C^6H^3ClSO_3Na$ , forms colourless needles, often united in groups. The *lithium salt*,  $C^6H^3ClSO_3Li + H_2O$ , crystallises in granular aggregates, extremely soluble in water. The *ammonium salt*,  $C^6H^3ClSO_3NH_4$ , forms long, glistening needles. The *barium salt*,  $(C^6H^3ClSO_3)_2Ba$ , crystallises in crusts or aggregates of small needles, difficultly soluble in water; on adding barium hydrate to its solution, the *dibarium salt*,  $(C^6H^3ClSO_3)_2Ba + 4H_2O$ , is precipitated in small glistening needles, very difficultly soluble in water. The *calcium salt*,  $(C^6H^3ClSO_3)_2Ca + 2H_2O$ , crystallises in easily



soluble needles; the *magnesium salt*,  $(C^6H^4ClSO^3)^2Mg + 6H^2O$ , in small flat plates, or pointed flat needles. The *copper salt*,  $(C^6H^4ClSO^3)^2Cu + 6H^2O$ , crystallises from alcohol in small, greenish-white needles, extremely soluble in water. *Potassium ethyl-parachlorophenolsulphonate*,  $C^6H^4Cl.OC^2H^5.SO^3K$ , forms fine, glistening needles, united in stars.

*β-Parachlorophenolsulphonic acid* or *Parachlorophenolmetasulphonic acid*.—The potassium *β*-chlorophenolsulphonate,  $C^6H^4SO^3K$ , crystallising in regular stellate groups of short prisms, which Petersen a. Predari obtained (1st Suppl. 924) in small quantity from the acid prepared by adding parachlorophenol to fuming sulphuric acid, and allowing the mixture to stand for some days without heating, was perhaps derived from this acid. It was not obtained when the mixture of phenol and acid was heated. It is somewhat less soluble than potassium *α*-parachlorophenolsulphonate; the solution is a deep-violet; nitric acid converts it into parachloro-*β*-dinitrophenol (m. p. 81°). On fusion with potassium hydrate, it furnishes pyrogallol in small quantity.

*Orthochlorophenolsulphonic acids*.—According to Kramers (*Ann. Ch. Pharm.* clxxiii. 331) the action of sulphuric acid on orthochlorophenol (1 : 2) produces two isomeric sulpho-acids, which he terms *γ*- and *δ*-chlorophenolsulphonic acid. The *δ*-acid is produced in relatively small quantity, together with the *γ*-acid, when the chlorophenol is gradually added to a carefully cooled mixture of 1 pt. of fuming with 1–2 pts. of ordinary sulphuric acid; the *γ*-acid alone is produced if the cooling be omitted, or if fuming sulphuric acid only is employed. To separate the two acids, the product is poured into water, and milk of lime is added to alkaline reaction; the concentrated filtrate is placed over sulphuric acid, when after some days small needles of the *δ*-dicalcium salt separate, and afterwards, the much more soluble dicalcium salt of the *γ*-acid separates from the mother-liquor in botryoidal masses.

*Orthochlorophenolparasulphonic acid* or *γ-Chlorophenolsulphonic acid*,  $C^6H^4Cl.OH.SO^3H$  (1 : 2 : 4). This acid crystallises from the concentrated aqueous solution in small colourless plates, or from a less concentrated solution placed over sulphuric acid, in small cubes containing 1 mol. of water. It begins to decompose at 80°; with ferric chloride it yields a magnificent violet colour. *Potassium orthochlorophenolparasulphonate*,  $C^6H^4ClSO^3K + \frac{1}{2}H^2O$ , forms large, colourless, apparently triclinic prisms; one part of the anhydrous salt dissolves in 7.11 pts. of water at 9°. It is converted by dilute nitric acid into potassium orthochlorororthonitrophenolparasulphonate, which on further treatment with nitric acid yields chloro-*α*-dinitrophenol, melting at 110°–111° (Armstrong). The *dipotassium salt*,  $C^6H^4ClSO^3K^2 + 3\frac{1}{2}H^2O$ , crystallises in deliquescent leaf-like forms, united together. The *monosodium salt*,  $C^6H^4ClSO^3Na + 11\frac{1}{2}H^2O$ , is so extremely soluble in water and alcohol, that it cannot be obtained in the crystallised state; the *disodium salt*,  $C^6H^4ClSO^3Na^2 + 3H^2O$ , separates in indistinct white crystals, extremely soluble in water, but almost insoluble in alcohol. The *monocalcium salt*,  $(C^6H^4ClSO^3)^2Ca + 11\frac{1}{2}H^2O$ , forms small white crystals, very soluble in water and alcohol; the *dicalcium salt*,  $(C^6H^4ClSO^3)^2Ca^2 + 71\frac{1}{2}H^2O$ , crystallises in white aggregates, which soon effloresce when exposed to the air; 1 pt. of the anhydrous salt dissolves in 2.64 pts. of water at 12°; it is almost insoluble in alcohol. The *monobarium salt*,  $(C^6H^4ClSO^3)^2Ba + 11\frac{1}{2}H^2O$ , separates in small white crystals united in granular aggregates. The *lead salt*,  $(C^6H^4ClSO^3)^2Pb + 4H^2O$ , crystallises in small, hard, rhombic crystals, soluble in water and alcohol; it is decomposed when heated above 130°, with evolution of chlorophenol; the *di-salt*,  $(C^6H^4ClSO^3)^2Pb^2 + 2H^2O$ , separates as a white powder difficultly soluble in cold water, and insoluble in alcohol. Basic lead salts of variable composition are also readily produced. The *copper salt*,  $(C^6H^4ClSO^3)^2Cu + 4H^2O$ , forms blue-green rhombic prisms, which are decomposed when heated above 120°.

*δ-Chlorophenolsulphonic acid*,  $C^6H^4Cl.OH.SO^3H$ .—The *monopotassium salt*,  $C^6H^4ClSO^3K$ , crystallises in small plates. The *dicalcium salt*,  $(C^6H^4ClSO^3)^2Ca^2 + 4H^2O$ , forms small needles; 1 pt. of the anhydrous salt dissolves in 44.68 pts. of water at 11°; it is insoluble in alcohol.

*Parachlorophenoldisulphonic acid*,  $C^6H^4Cl.OH.(SO^3H)^2$ .—An acid of this composition was obtained by Petersen a. Baehr-Predari by heating parachlorophenol with sulphuric acid, but not examined; the barium salt is very difficultly soluble in water.

*Diorthochlorophenolparasulphonic acid*,  $C^6H^4Cl^2.OH.SO^3H$  (1 : 2 : 4 : 6), which was first prepared by Kolbe a. Gauke (1st Suppl. 924), may be produced by the action of sulphuric acid on Seifart's diorthochlorophenol (*ibid.* 908; Armstrong). The action of nitric acid on this acid and its potassium salt have been investigated at length by Faust (*Zell. f. Chem.* 1871, 338) and by Armstrong (*Chem. Soc. J.* [2], ix. 1112).



**Orthochloroparachlorophenolorthosulphonic acid**,  $C^6H^3Cl^2.OH.SO^3H$  (1 : 2 : 4 : 6).—This compound is produced when chlorine acts upon phenolorthosulphonic acid (Faust; Armstrong), and by the action of sulphuric acid or chlorhydric sulphate on the dichlorophenol melting at  $42^\circ-43^\circ$  (Armstrong, *Chem. Soc. J.* [2], x, 93). The metallic salts of this acid have not yet been examined. By the action of nitric acid it is readily converted into dichlororhthonitrophenol (m. p.  $121^\circ$ ).

**Trichlorophenolsulphonic acid**.—Trichlorophenol dissolves in warm fuming sulphuric acid, and the solution solidifies on cooling to a mass of crystals (Kekulé, *Org. Chem.* iii, 233). When chlorhydric sulphate is added to trichlorophenol, hydrochloric acid is evolved; the product dissolves in great part in water, but on standing, trichlorophenol separates from the solution, in consequence, it would appear, of the gradual decomposition of the sulpho-acid (Armstrong).

**Bromophenolsulphonic Acids**. **Bromophenolparasulphonic acid**,  $C^6H^3Br.OH.SO^3H$ .—The potassium salt of this acid is formed in relatively small quantity, together with potassium dibromophenolparasulphonate, on adding 1. mol. of bromine to a cold aqueous solution of 1 mol. of potassium phenolparasulphonate (Senhofer, *Ann. Chem. Pharm.* clvi, 102). Potassium bromophenolparasulphonate crystallises in prisms; its aqueous solution is coloured a pale violet by ferric chloride, and is precipitated by basic lead acetate.

**Bromophenolorthosulphonic acid**.—The potassium derivative of this compound is formed in a similar manner from potassium phenolorthosulphonate (Senhofer); and crystallises in pointed needles; its solution is precipitated by lead acetate. The barium salt is moderately soluble in hot water, and crystallises in anhydrous forms; the copper salt is also anhydrous.

**Diorthobromophenolparasulphonic acid**,  $C^6H^2Br^2.OH.SO^3H$  (1 : 2 : 4 : 6).—The potassium derivative of this acid may be obtained in theoretical quantity by the action of 2 mols. of bromine on a cold dilute aqueous solution of 1 mol. of potassium phenolparasulphonate (Senhofer, *loc. cit.*; Armstrong a. Brown, *Chem. Soc. J.* 1872, 857). The free acid crystallises in small rectangular plates; its solution is coloured pale violet by ferric chloride, and is not precipitated by normal lead acetate, although it is precipitated by basic acetate. The potassium salt,  $C^6H^2Br^2.SO^3K$ , crystallises in anhydrous plates, or in long needles with 1 mol. of water; it is difficultly soluble in cold water. The dipotassium salt,  $C^6H^2Br^2.SO^3K^2 + 2H^2O$ , crystallises from a concentrated solution in elongated plates. The sodium salt,  $C^6H^2Br^2.SO^3Na + 2H^2O$ , forms long, brilliant, white needles, easily soluble in hot, but difficultly soluble in cold water. The barium salt,  $(C^6H^2Br^2.SO^3)^2Ba + 2H^2O$ , crystallises in long, fine, silky needles, very difficultly soluble in cold water; the dibarium salt,  $(C^6H^2Br^2.SO^3)^2Ba^2 + 8H^2O$ , forms long needles, more soluble in water than the monobarium salt. Potassium dibromophenolparasulphonate yields potassium nitrobromophenolparasulphonate, dibromoparanitrophenol (m. p.  $141^\circ$ ), and bromo- $\alpha$ -dinitrophenol (m. p.  $117^\circ$ ), on treatment with nitric acid (Armstrong a. Brown).

The dibromophenolsulphonic acid which Schmitt (*Ann. Chem. Pharm.* cxx, 181) obtained from dibromosulphanilic acid by Griess's method is probably diorthobromophenolsulphonic acid.

**Parabromorhthobromophenolorthosulphonic acid**,  $C^6H^2Br^2.OH.SO^3H$  (1 : 2 : 4 : 6).—Potassium dibromophenolorthosulphonate is produced, together with some tribromophenol, when bromine is added to an aqueous solution of potassium phenolorthosulphonate (Senhofer; Armstrong a. Brown). It is also formed by the action of 1 mol. of bromine on a solution of 1 mol. of potassium orthobromophenolorthoparadisulphonate (Armstrong, *Chem. Soc. J.* 1872, 867). The free acid crystallises in concentrically-grouped needles; the aqueous solution is coloured an intense violet by ferric chloride, and is precipitated by normal lead acetate. The potassium salt crystallises in fine anhydrous needles; the dipotassium salt separates from dilute alcohol in long glistening plates. The barium salt forms difficultly soluble anhydrous plates; the dibarium salt is also anhydrous. The cadmium salt,  $C^6H^2Br^2.SO^3Cd + 1\frac{1}{2}H^2O$ , crystallises in very soluble yellow plates. The lead salt,  $C^6H^2Br^2.SO^3Pb$ , separates as a white precipitate on the addition of lead acetate to a solution of the potassium salt.

Potassium dibromophenolorthosulphonate is converted by nitric acid into dibromorhthonitrophenol (m. p.  $117^\circ$ ).

**Orthobromophenolorhthoparadisulphonic acid**,  $C^6H^3Br.OH.(SO^3H)^2$  (1 : 2 : 4 : 6).—The potassium salt of this acid is prepared by the action of 1 mol. of bromine on a cold aqueous solution of 1 mol. of potassium phenoldisulphonate (1st Suppl, 926); it is very soluble in hot, and moderately in cold water, and crystallises in needles or tufts of short flat blades, which rapidly disintegrate to a snow-white anhydrous powder on exposure to the air. It is not precipitated, except in very con-

centrated solutions, by barium chloride. It is violently acted upon by nitric acid yielding potassium bromonitrophenolsulphonate, bromo-*o*-dinitrophenol, and trinitrophenol, in proportions which vary with the strength of the acid employed (Armstrong, *Chem. Soc. J.* 1872, 866).

*Diiodophenolparasulphonic acid*,  $C^6H^2I^2.OH.SO^3H$ , is formed by the action of iodine and mercuric oxide on an alcoholic solution of phenolparasulphonic acid (Armstrong). The *potassium salt*,  $C^6H^2I^2.SO^3K + 2H^2O$ , crystallises in long pink needles; the *barium salt*,  $(C^6H^2I^2.SO^3)^2Ba + 4H^2O$ , forms long, flat needles.

**Nitrophenolsulphonic Acids.** *Paranitrophenolorthosulphonic acid*,  $C^6H^3.OH.NO^2.SO^3H$  (1 : 2 : 4).—Körner a. Post have obtained this acid by acting upon paranitrophenol with fuming sulphuric acid (*Deut. Chem. Ges. Ber.* v. 852, 1055; vi. 395; vii. 163; *Chem. Soc. J.* 1873, 757). The perfectly dry paranitrophenol is added to the acid and the mixture heated several hours in the water bath; if the nitrophenol be wet, and consequently much heat be evolved on adding it to the acid, secondary products are largely formed. The mixture is poured into water, neutralised with calcium carbonate, and filtered; barium chloride is then added to the filtrate, whereby barium nitrophenolsulphonate is precipitated, from which the free acid and other salts may readily be prepared. Paranitrophenolorthosulphonic acid,  $C^6H^3.OH.NO^2.SO^3H + 3H^2O$ , crystallises in slender needles or large well-formed colourless prisms, very soluble in water. The *potassium salt*,  $C^6H^3.OH.NO^2.SO^3K$ , crystallises in colourless prisms, slightly soluble in water; the *dipotassium salt*,  $C^6H^3.OK.NO^2.SO^3K + H^2O$ , in orange-coloured prismatic needles which are very soluble in water. The *sodium salt*,  $C^6H^3.OH.NO^2.SO^3Na + 2H^2O$ , forms colourless crystals; the *disodium salt*,  $C^6H^3.ONa.NO^2.SO^3Na + 2H^2O$ , yellow crystals. The *calcium salt*,  $(C^6H^3.NO^2.SO^3)^2Ca + 5H^2O$ , crystallises in aggregates of yellow needles; the *barium salt*,  $(C^6H^3.NO^2.SO^3)^2Ba + 2H^2O$ , in yellow prisms.

*Orthonitrophenolparasulphonic acid*,  $C^6H^3.OH.NO^2.SO^3H$  (1 : 2 : 4).—The potassium and sodium salts of this acid (1st Suppl. 925) are most readily obtained by the action of dilute nitric acid on potassium and sodium phenolparasulphonate (Schmitt a. Glutz, *Deut. Chem. Ges. Ber.* ii. 51; Körner, *Gazzetta chimica italiana*, 1872, ii. 444). Together with this acid, there appears to be produced a small quantity of an isomeric compound when it is prepared by the action of sulphuric acid on orthonitrophenol (Armstrong a. Brown, *Deut. Chem. Ges. Ber.* vii. 923).

*Dinitrophenolsulphonic acids*,  $C^6H^3.OH.(NO^2)_2.SO^3H$ .—According to Post (*ibid.* vii. 1323) both the above-described nitrophenolsulphonic acids may be converted into corresponding dinitrophenolsulphonic acids by careful nitration. He states also that phenoldisulphonic acid yields a dinitrophenolsulphonic acid on nitration.

**Amidophenolsulphonic Acids.** *Paramidophenolorthosulphonic acid*,  $C^6H^3.OH.NH^2.SO^3H$  (1 : 2 : 4), is produced on adding paramidophenol hydrochloride to fuming sulphuric acid, in which it dissolves with evolution of heat; the mixture is heated a short time on the water-bath, and then poured into water, when almost the whole of the paramidophenolorthosulphonic acid separates as a snow-white powder (Post, *ibid.* vi. 397). The same compound appears to be obtained on reducing paranitrophenolorthosulphonic acid with tin and hydrochloric acid (Post), and it is also formed by the action of sulphurous acid or sodium-hydrogen sulphite on dichloropara-diazophenol (Schmitt a. Bennewitz). It crystallises in minute cubes and fine soft silky needles; the cubes, which first separate from the hot solution, but in a relatively very small quantity, are probably anhydrous, whereas the needles contain 1 mol. of water. It is very slightly soluble in cold water, 1 pt. requiring for solution about 2,800 pts. of water at 15°. A slight decomposition takes place on boiling the solution, which assumes a dark-red colour, but this is entirely prevented by the presence of a reducing agent, such as sulphurous acid or stannous chloride. Paramidophenolorthosulphonic acid does not combine with acids, but yields metallic salts; these salts, however, are readily decomposed, and it is not possible to obtain them pure from the acid and the metallic carbonates. The *barium salt*,  $(C^6H^3.NH^2.SO^3)^2Ba$ , is obtained on the addition of barium chloride to an ammoniacal solution of the acid in the form of a crystalline precipitate, consisting of aggregates of small plates.

*Orthoamidophenolparasulphonic acid*,  $C^6H^3.OH.NH^2.SO^3H$  (1 : 2 : 4), is obtained by the action of sulphuric acid on orthoamidophenol hydrochloride (Post, Bennewitz), and on reduction of orthonitrophenolparasulphonic acid (Post). It crystallises in large colourless crystals like those of calc spar, containing  $\frac{1}{2}$  mol. of water; it is more soluble than its isomeride, water at 14° dissolving about .01 p.c. The aqueous solution decomposes on evaporation, unless this be conducted in an atmosphere of hydrogen.

**Diazophenolsulphonic Acids.** The above-described amidophenolsulphonic acids are converted into the corresponding diazo-acids when suspended in water and treated with nitrous acid (Bennewitz, *J. pr. Chem.* [2], viii. 52). *Paradiazophenolorthosulphonic acid*,  $C^6H^3\begin{matrix} N=N-OH \\ OH \\ SO^3H \end{matrix}$ , crystallises in colourless or pink glistening

rhombic plates; it is difficultly soluble in cold, but more soluble in hot water; and it may be crystallised from the hot aqueous solution, which, however, gradually becomes red on boiling. The same compound is obtained on dissolving the amido-acid in nitric acid, and on warming it with nitric acid and urea. It is reconverted by the action of nascent hydrogen on an acid solution into the amido-acid. It does not unite with acids, but furnishes with bases a series of highly unstable salts decomposing even in the cold.

The diazo-acid from orthoamidophenolparasulphonic acid crystallises in yellowish needles; it is far more soluble in water, and much less stable than the para-diazo-compound.

**Chloronitrophenolsulphonic Acids.** *Potassium parachlororthonitrophenolorthosulphonate*,  $C^6H^2Cl.NO^2.OH.SO^3K$ , is obtained by the action of dilute nitric acid on potassium parachlororthosulphonate; it crystallises in yellow needles, difficultly soluble in cold water. It is converted by nitric acid into chloro- $\beta$ -dinitrophenol (m. p. 81°). The *dipotassium salt*,  $C^6H^2Cl.NO^2.OK.SO^3K$ , forms magnificent long red needles, easily soluble in water (Armstrong a. Prevost, *Deut. Chem. Ges. Ber.* vii. 404).

*Potassium orthochlororthonitrophenolparasulphonate*,  $C^6H^2Cl.NO^2.OH.SO^3K + \frac{1}{2}H^2O$ , is formed by the action of weak nitric acid on potassium diorthochlorophenolparasulphonate; it crystallises in tufts of pale-yellow silky needles, very soluble in warm water, slightly soluble in cold. It yields chloro- $\alpha$ -dinitrophenol (m. p. 110°–111°) on treatment with nitric acid, and is converted into dichlororthonitrophenol (m. p. 121°) by the action of chlorine on its aqueous solution. The *dipotassium salt*,  $C^6H^2Cl.NO^2.OK.SO^3K$ , crystallises in orange-red six-sided plates, extremely soluble in hot water, moderately in cold (Armstrong, *Chem. Soc. J.* 1871, 1117). The potassium chlorophenolsulphonate obtained by Armstrong a. Prevost, by acting on potassium orthochlorophenolparasulphonate with weak nitric acid, is probably the same compound. A chlororthonitrophenolparasulphonic acid is produced by the action of chlorine on an alcoholic solution of orthonitrophenolparasulphonic acid, but has not yet been fully examined (Armstrong a. Brown, *ibid.* 1872, 872).

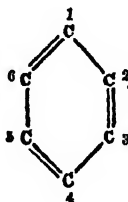
**Bromonitrophenolsulphonic Acids.** The potassium salts of bromonitrophenolsulphonic acids have been obtained: 1. By the action of nitric acid on potassium diorthobromophenolparasulphonate. 2. By similar treatment of potassium orthobromophenolparaorthodisulphonate. 3. By the action of bromine on an alcoholic solution of the orthonitrophenolsulphonic acids. 4. By nitrating the potassium salts of parabromo- and orthobromophenolsulphonic acids (Armstrong; Armstrong a. Brown; Armstrong a. Prevost, *Chem. Soc. J.* 1872, 857–872; *Deut. Chem. Ges. Ber.* vii. 404, 924). 5. By acting on an alcoholic solution of paranitrophenolorthosulphonic acid (Post, *ibid.* vii. 169) with bromine. These compounds have as yet, however, been comparatively little studied.

**Iodonitrophenolsulphonic Acids.** *Orthiodorthonitrophenolparasulphonic acid*,  $C^6H^2I.NO^2.OH.SO^3H$  (1 : 2 : 4 : 6), is produced when iodine and mercuric oxide are added to an alcoholic solution of orthonitrophenolparasulphonic acid (Armstrong a. Brown, *Chem. Soc. J.* 1872, 869). The *potassium salt*,  $C^6H^2I.NO^2.OH.SO^3K$ , crystallises in difficultly soluble yellow scales, much resembling chlornil; these consist of aggregates of short needles; it is converted into potassium orthobromorthonitrophenolparasulphonate by the action of 1 mol. of bromine. The *dipotassium salt*,  $C^6H^2I.NO^2.OK.SO^3K$ , forms deep red prisms easily soluble in water. The *barium salt*,  $(C^6H^2I.NO^2.SO^3)^2Ba + 4H^2O$ , is precipitated in the form of pale yellow silky needles on the addition of barium chloride to a solution of the potassium salt.

*Orthiodoparanitrophenolorthosulphonic acid*,  $C^6H^2I.NO^2.OH.SO^3H$  (1 : 2 : 4 : 6), is formed, together with diorthiodoparanitrophenol (m. p. 157°), by the action of iodine and mercuric oxide on an alcoholic solution of paranitrophenolorthosulphonic acid (Post a. Brackebusch, *Deut. Chem. Ges. Ber.* vii. 167). The *calcium salt*,  $(C^6H^2I.NO^2.SO^3)^2Ca^2 + 6H^2O$ , forms coarse yellow needles. The *dibarium salt* crystallises in long yellow needles; the *ammonium salt* is difficultly soluble in water; the *lead salt* is obtained as a yellow crystalline precipitate on the addition of lead acetate to a solution of the calcium salt.

## 'CONSTITUTION' OF THE PHENOL DERIVATIVES.

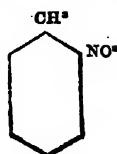
The prefix *ortho* was originally applied by Körner, in the case of the isomeric di-derivatives of benzene, simply to denote the compound which formed the chief product of the action of a reagent on a mono-derivative of benzene; thus he found that the chief product of the action of iodine on phenol was an iodophenol yielding hydroquinone on fusion with potassium hydrate; to this he gave the name orthiodophenol, and it became the practice to term all such di-derivatives as could be more or less directly referred to hydroquinone, *ortho*-derivatives. The iodophenol which he succeeded in obtaining from the so-called paranitraniline formed from ordinary dinitrobenzene, gave resorcin on fusion with potassium hydrate, and consequently resorcin, and all bodies which were considered as belonging to the same series of isomerides, were termed *para*-derivatives. The third iodophenol, formed in small quantity together with orthiodophenol, gave pyrocatechin on fusion with potassium hydrate; pyrocatechin and those di-derivatives which could be classed in a series with it were then termed *meta*-derivatives. Later on it became usual to associate with the terms *ortho*, *para*, and *meta*, certain conceptions as to the relative positions occupied by the radicles which had been introduced in place of hydrogen into benzene, Kekulé's theory of the 'constitution' of benzene being taken as the basis of argument, and the 'positions' denoted by figures; thus:



Graebe's researches on naphthalene (1st Suppl. 198 n. 212) led to the assumption that in phthalic acid,  $C^6H^2(COOH)^2$ , the two carboxyls are in the position 1 : 2, and Baeyer pointed out that the formation of mesitylene,  $C^6H^2(CH^3)^3$ , from acetone necessitates the assumption that the three methyl-groups occupy the positions 1 : 3 : 5, and hence that isoxylene,  $C^6H^4(CH^3)^2$ , which yields isophthalic acid on oxidation, has the methyl-groups in the position 1 : 3; accordingly, since phthalic acid is 1 : 2, and isophthalic, 1 : 3, terephthalic acid is of necessity 1 : 4. Hydroquinone, pyrocatechin, and resorcin were then considered to belong respectively to the same series as phthalic acid, isophthalic acid, and terephthalic acid, and these three acids have gradually usurped the place of the three dioxybenzenes as standards of reference, members of the phthalic or 1 : 2 series being commonly termed *ortho*-derivatives, those of the isophthalic or 1 : 3 series, *meta*-derivatives, and those of the terephthalic or 1 : 4 series, *para*-derivatives. Körner, however, is singular in using these prefixes in an opposite sense: thus he terms the 1 : 4 derivatives *ortho*-compounds, the 1 : 3 derivatives *para*-compounds, and the 1 : 2 derivatives *meta*-compounds (*Gazzetta chimica italiana*, 1874, 316).

All recent researches tend to confirm the hypothesis that the carboxyls in phthalic, isophthalic, and terephthalic acids are respectively in the positions 1 : 2 or 1 : 6, 1 : 3 or 1 : 5, and 1 : 4 (see Ladenburg, *Deut. Chem. Ges. Ber.* ii. 140; v. 322; vii. 1133 n. 1684), but have necessitated the shifting of many compounds considered to belong to one or another of these three series; thus resorcin has been shown to belong to the isophthalic (1 : 3) series, and not to the terephthalic (1 : 4) series. Again, hydroquinone, which was long considered a member of the phthalic (1 : 2) series, is now placed in the 1 : 4 series. The proof that resorcin belongs to the isophthalic series is as follows. When toluene is nitrated, two nitrotoluenes are formed which it has been proved belong respectively to the *ortho* (1 : 2) and *para* (1 : 4) series, and both of these yield the same dinitrotoluene on further nitration; this dinitrotoluene consequently has the constitution 1 : 2 : 4; thus:

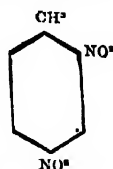
\* It must not be forgotten that the *ortho*- and *meta*-positions are repeated, since the positions 2 and 6 correspond respectively to the positions 6 and 2.



Orthonitrotoluene.

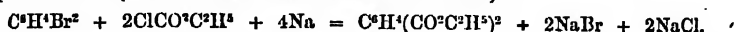


Paranitrotoluene.



Orthoparanitrotoluene.

On oxidation dinitrotoluene furnishes a dinitrobenzoic acid which, on reduction, yields a diamidobenzene identical with that which is obtained by reducing dinitrobenzene; hence it follows that the nitro-groups in dinitrotoluene and dinitrobenzene are in relatively the same positions, i.e. 1 : 3 (Wurster, *Deut. Chem. Ges. Ber.* vii. 148). Dinitrobenzene may, however, as Körner has shown, readily be converted into resorcin, which consequently is also a member of the isophthalic (1 : 3) series. The connection of ordinary dinitrobenzene with isophthalic acid is further proved by the fact that the dibromobenzene (b. p. 219°), which may be obtained from the former by Griess's method (Körner, *Gazzeta chimica italiana*, 1874, 331), is converted by the action of sodium and ethyl chlorocarbonate, and subsequent saponification of the product, into isophthalic acid (Wurster, *Deut. Chem. Ges. Ber.* vi. 1486):



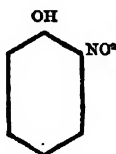
**Nitrophenols.**—One of the three nitrophenols is obtained from diinitrobenzene; it therefore belongs to the isophthalic (1 : 3) series.

The connection of the non-volatile nitrophenol (m. p. 110°) obtained on nitration of phenol with the terephthalic (1 : 4) series, is proved in a variety of ways. Thus it has been shown that crystalline dibromobenzene (m. p. 89°) is converted by the action of methyl iodo and sodium into a dimethyl-benzene yielding terephthalic acid on oxidation (v. Meyer, *Ann. Chem. Pharm.* clvi. 281); but crystalline dibromobenzene may be formed, by Griess's method, from the bromonitrobenzene (m. p. 125°) produced on nitrating bromobenzene, and from this bromonitrobenzene, nitrophenol (m. p. 110°) is readily produced by heating with potassium hydrate solution (v. Richter). Nitrophenol (m. p. 110°), as Salkowski has shown, may be converted into anisic acid, and hence into paraoxybenzoic acid, which, there can be no doubt, is a member of the terephthalic series. The connection of hydroquinone with the terephthalic series is therefore proved by the observation that it may be produced from paranitrophenol (Salkowski).

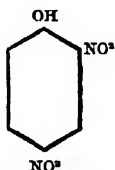
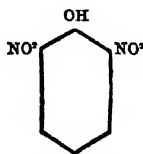
The above considerations show that the third nitrophenol (m. p. 46°) must of necessity belong to the phthalic (1 : 2) series; and direct proof of this is afforded by its conversion into the diamidobenzene melting at 99° (Salkowski), which has been proved to be a member of that series. Moreover, this assumption is the only one which enables us to account for the formation of  $\alpha$ -dinitrophenol from it and from paranitrophenol, and the fact that both  $\alpha$ - and  $\beta$ -dinitrophenol yield ordinary dinitrobenzene (1 : 3) when the OH group is removed. This is at once evident on inspection of the following symbols:



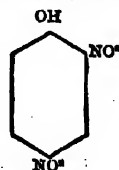
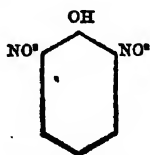
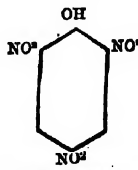
Paranitrophenol.



Orthonitrophenol.


 $\alpha$ -Dinitrophenol.

 $\beta$ -Dinitrophenol.

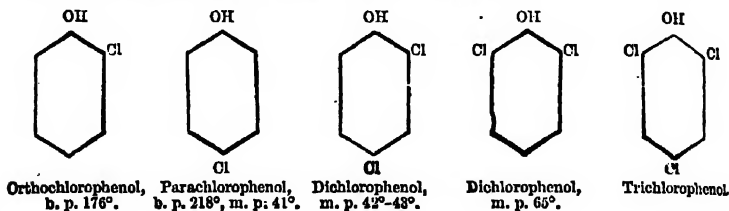
The constitution of  $\alpha$ - and  $\beta$ -dinitrophenol results from the observation that it is produced by nitration of  $\alpha$ - and  $\beta$ -dinitrophenol:


 $\alpha$ -Dinitrophenol.

 $\beta$ -Dinitrophenol.


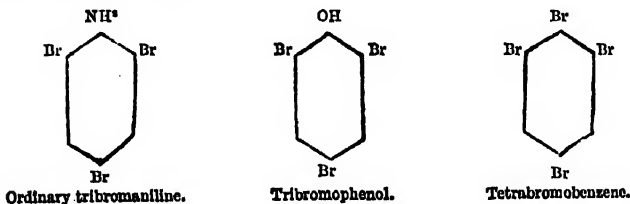
Trinitrophenol.

**Chloro- and Bromophenols.**—Two of the monochlorophenols have been obtained from nitrophenols by displacing the nitro-group by chlorine, and thus the position of the chlorine determined. The three monochloroanilines have also been converted into the three corresponding chlorophenols, and the monobromophenols have been similarly prepared from the three monobromoanilines.

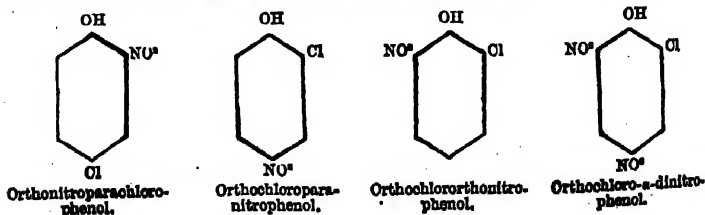
The constitution of the dichlorophenol melting at  $42^{\circ}$ – $43^{\circ}$  is shown to be 1 : 2 : 4 by its formation from ortho- and para-chlorophenol, and that of the isomeric compound (m. p.  $65^{\circ}$ ) to be 1 : 2 : 6, because it may be obtained from the dichloroparanitrophenol, which it will be shown later on is 1 : 2 : 4 : 6. Since both of these yield trichlorophenol on chlorination, this becomes 1 : 2 : 4 : 6 ; thus :



Ordinary dibromophenol corresponds with the dichlorophenol melting at  $42^{\circ}$ – $43^{\circ}$ , and tribromophenol with trichlorophenol; this conclusion with regard to tribromophenol is confirmed by its conversion, when acted upon by phosphorus pentabromide, into the same tetrabromobenzene as may be obtained by displacing the  $\text{NH}_2$  group of ordinary tribromoaniline by bromine; thus :

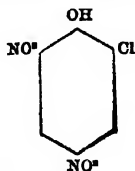


**Chloronitro-, Bromonitro-, and Iodonitrophenols.**—Since the chloro- and bromo-nitrophenols have been obtained on the one hand by nitrating the chloro- and bromo-phenols, and on the other by chlorinating or brominating the nitrophenols, we may readily infer their constitution, since the constitution of the nitro-, chloro-, and bromo-phenols is known. One or two examples will suffice in illustration:—Parachlorophenol yields, on nitration, a parachloronitrophenol (m. p.  $86^{\circ}$ ) identical with one that is formed on chlorinating orthonitrophenol; it is therefore *parachloro-orthonitrophenol*. Paranitrophenol furnishes, when chlorinated, an isomeric paranitrochlorophenol (m. p.  $110^{\circ}$ ), which may be obtained by nitrating orthochlorophenol, and is therefore *paranitro-ortho-chlorophenol*. A third nitrochlorophenol (m. p.  $70^{\circ}$ ) is obtainable by nitration of orthochlorophenol, and since on further nitration it is converted into orthochloro- $\alpha$ -dinitrophenol, which is also obtained by nitrating orthochloroparanitrophenol, it must of necessity be an *ortho-chloro-orthonitrophenol*; thus :

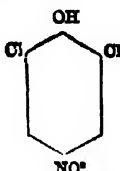


Since the dichloronitrophenol obtained on chlorinating paranitrophenol may be converted, by displacing one of the atoms of chlorine by  $\text{NO}_2$  by the action of nitric acid, into orthochloro- $\alpha$ -dinitrophenol, it follows that the two chlorine-atoms occupy in it the positions 2 and 6, and that consequently this also is the position of the chlorine-

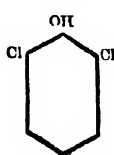
atoms in the dichlorophenol (m. p. 65°), which is obtained on removing the nitro-group from paranitrodichlorophenol; thus:



Orthochloro- $\alpha$ -dinitrophenol.

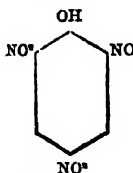


Dichloroparanitrophenol.

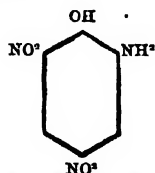


Diorthochlorophenol (m. p. 65°).

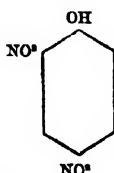
The constitution of iodo- $\alpha$ -dinitrophenol is given by the following observations: 1. It may be obtained by iodating  $\alpha$ -dinitrophenol, and 2. By the action of hydriodic acid on diazodinitrophenol from amidodinitrophenol or picramic acid, it being proved that it is one of the nitro-groups in the *ortho*-position which undergoes reduction when trinitrophenol is converted into amidodinitrophenol, by the fact that when amidodinitrophenol is converted into dinitrophenol by the action of ethyl nitrite,  $\alpha$ -dinitrophenol is obtained; thus:



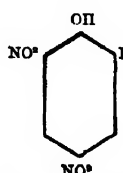
Trinitrophenol.



Amidodinitrophenol.

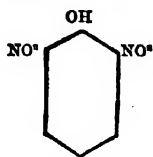


$\alpha$ -Dinitrophenol.

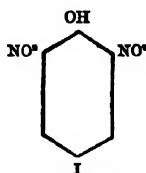


Iodo- $\alpha$ -dinitrophenol.

In the case of iodo- $\beta$ -dinitrophenol the position of the nitro-group is given by its formation from  $\beta$ -dinitrophenol; the position of the iodine has not been directly established, but there can be no doubt that it is in the *para*-position, since the corresponding chloro- and bromo-dinitrophenols obtained by chlorinating and brominating  $\beta$ -dinitrophenol are also produced by nitrating parachloro- and parabromophenol:



$\beta$ -Dinitrophenol.

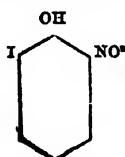


Iodo- $\beta$ -dinitrophenol.

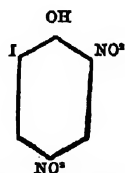
The iodonitrophenol melting at 93° can only be orthiodoparanitrophenol, since it is converted into iodo- $\alpha$ -dinitrophenol on nitration; and since the isomeride melting at 109°-110°, produced from orthonitrophenol, also yields iodo- $\alpha$ -dinitrophenol on nitration, it is probably also an orthiodophenol derivative; thus:



Iodonitrophenol (m. p. 93°).



Iodonitrophenol (m. p. 109°).

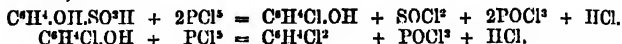


Iodo- $\alpha$ -dinitrophenol.

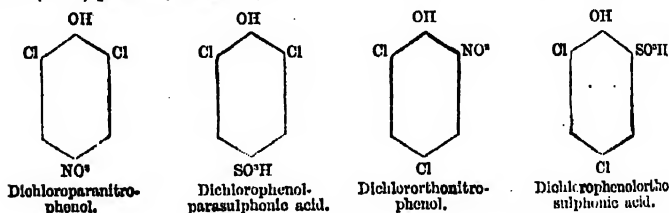
**Phenolsulphonic acids.**—Of the two modifications of phenolsulphonic acid, the unstable modification is apparently shown to belong to the *ortho*-series (1 : 2) by its conversion into pyrocatechin on fusion with potassium hydrate. The isomeric acid (Kekulé's phenolparasulphonic acid) furnishes resorcin on similar treatment, but only in very small quantity; the conclusion that it belongs to the same series as resorcin

is therefore not justified by this result, especially as recent observations have shown that the reaction with fused potassium hydrate is not in all cases a trustworthy means of determining the constitution of a compound. Thus two isomeric bromophenols yield the same diorybenzene (resorcin) on fusion with potassium hydrate, and, on the other hand, two different observers have obtained different products from the same chlorophenol, Petersen having converted parachlorophenol into hydroquinone by fusing it with potassium hydrate, whereas Faust obtained resorcin. It has also recently been stated that the three isomeric bromobenzenesulphonic acids furnish resorcin on fusion with potassium hydrate (Limpricht, *Deut. Chem. Ges. Ber.* vii. 1352).

Kekulé's phenolparasulphonic acid is shown, however, to belong to the terephthalic (1 : 4) series by its conversion into parachlorophenol and paradichlorobenzene (m. p. 53°-54°), on distillation with phosphorus pentachloride (Barbuglia a. Kekulé, *ibid.* v. 875; vi. 943):



Assuming that when the haloïd-derivatives of the phenolsulphonic acids are converted into haloïd-nitrophenols by the action of nitric acid, the sulpho-group,  $\text{SO}^2\text{H}$ , is directly displaced by the  $\text{NO}^2$ -group--and there is every reason to suppose that this is the case--the fact that the dichlorophenolsulphonic obtained from Kekulé's phenolparasulphonic acid yields, on nitration, a dichloronitrophenol identical with that obtained on chlorinating paranitrophenol, also proves that the sulpho-group in the acid in question is in the para-position. Similarly, since Kekulé's phenolmetasulphonic acid yields, when chlorinated, a dichlorophenolsulphonic acid which furnishes dichlororthonitrophenol on nitration, the sulpho-group in this acid may be supposed to occupy the ortho- (1 : 2) position; thus:



Phenoldisulphonic acid is shown to be 1 : 2 : 4 by its formation from phenolortho- and phenolpara-sulphonic acid.

The constitution of the haloïd and haloïd-nitro-phenolsulphonic acids is inferred from their formation from the haloïd-phenols, &c., and from their conversion into haloïd-nitrophenols of known constitution by the action of nitric acid.

The various haloïd-, nitro-, sulpho-, haloïd-sulpho-, haloïd-nitro-, nitro-sulpho-, and haloïd-nitro-sulpho-phenols of known constitution, which have been obtained from phenol, are arranged in the following table (p. 929). Each compound is represented merely by the radicle or radicles, by the substitution of which for hydrogen in phenol it is formed.

This table contains, with one or two exceptions, all the mono-, di-, and tri-derivatives as yet prepared from phenol. The number of phenol-derivatives obtained by indirect methods, and not included in the table, is also extremely small.

It is at once evident that the results here tabulated lead to two remarkable conclusions, viz.—

1. That the action of the halogens, of nitric acid, and of sulphuric acid, on phenol is similar, inasmuch as the same hydrogen-atoms are always displaced.
2. That the tendency of these agents is always to displace hydrogen in the *ortho*-positions (1 : 2 and 1 : 6), and the *para*-position (1 : 4), and but rarely to produce *meta*-derivatives. Thus, although it results from Körner's observations that meta-bromophenol may be obtained directly from phenol, its formation appears to be dependent upon certain conditions not yet understood. It is also not known at present whether meta-iodophenol is a constant product of the action of iodine on phenol. It appears not improbable, however, that the tendency to form the meta-derivative may, in the case of iodine, be considerable, and thus always lead to its production; but less strong in the case of bromine, and still less so in the case of chlorine, so that meta-derivatives are not formed by these in any quantity, except under peculiar conditions. There is no evidence at present that with nitric or sulphuric acid there is any tendency to form meta-derivatives.



Abbreviated symbol of compound	Description	Position of the displacing radicals relatively to the OH-group which occupies the position 1				
		Ortho, 2	Meta, 3	Para, 4	Meta, 5	Ortho, 6
NO <sup>2</sup>	m. p. 45°	NO <sup>2</sup>	—	—	—	—
NO <sup>2</sup>	110°	—	—	NO <sup>2</sup>	—	—
NO <sup>2</sup> .NO <sup>2</sup>	64°	NO <sup>2</sup>	—	—	—	NO <sup>2</sup>
NO <sup>2</sup> .NO <sup>2</sup>	114°	NO <sup>2</sup>	—	NO <sup>2</sup>	—	—
NO <sup>2</sup> .NO <sup>2</sup> .NO <sup>2</sup>	122.5°	NO <sup>2</sup>	—	NO <sup>2</sup>	—	NO <sup>2</sup>
Cl	b. p. 176°	Cl	—	—	—	—
Cl	b. p. 218° m. p. 41°	—	—	Cl	—	—
Cl.Cl	m. p. 42°-43°	Cl	—	—	—	Cl
Cl.Cl	65°	Cl	—	Cl	—	—
Cl.Cl.Cl	67°	Cl	—	Cl	—	Cl
Br	From orthobromanilino	Br	—	—	—	—
Br	b. p. 227°-229°	—	Br	—	—	—
Br	m. p. 66°	—	—	Br	—	—
Br.Br	40°	Br	—	Br	—	—
Br.Br.Br	95°	Br	—	Br	—	Br
I	Liquid	(?) I	—	—	—	—
I	m. p. 89°	—	(?) I	—	—	—
I	64°-66°	—	—	(?) I	—	—
I.I	150°	I	—	I	—	—
I.I.I	156°	I	—	I	—	I
SO <sup>2</sup> H	Kekulé's phenolmeta- sulphonic acid	SO <sup>2</sup> H	—	—	—	—
SO <sup>2</sup> H	Kekulé's phenolpara- sulphonic acid	—	—	SO <sup>2</sup> H	—	—
SO <sup>2</sup> H.SO <sup>2</sup> H	—	SO <sup>2</sup> H	—	SO <sup>2</sup> H	—	—
Cl.NO <sup>2</sup>	m. p. 70°	NO <sup>2</sup>	—	—	—	Cl
Cl.NO <sup>2</sup>	86°	NO <sup>2</sup>	—	Cl	—	—
Cl.NO <sup>2</sup>	110°	Cl	—	NO <sup>2</sup>	—	—
Br.NO <sup>2</sup>	88°	Br	—	Br	—	—
Br.NO <sup>2</sup>	102°	Br	—	NO <sup>2</sup>	—	—
I.NO <sup>2</sup>	109°-110°	NO <sup>2</sup>	—	—	—	(?) I
I.NO <sup>2</sup>	93°-94°	I	—	NO <sup>2</sup>	—	—
NO <sup>2</sup> .SO <sup>2</sup> H	Kekulé a. Kolbe	NO <sup>2</sup>	—	SO <sup>2</sup> H	—	—
NO <sup>2</sup> .SO <sup>2</sup> H	Körner a. Post	SO <sup>2</sup> H	—	NO <sup>2</sup>	—	—
Cl.SO <sup>2</sup> H	Petersen a. Baehr- Prodari	Cl	—	SO <sup>2</sup> H	—	—
Cl.SO <sup>2</sup> H	Kramers	SO <sup>2</sup> H	—	Cl	—	—
Br.SO <sup>2</sup> H	From orthobromo- phenol (Armstrong)	Br	—	SO <sup>2</sup> H	—	—
Br.SO <sup>2</sup> H	From parabromophenol (Armstrong)	SO <sup>2</sup> H	—	Br	—	—
Cl.NO <sup>2</sup> .NO <sup>2</sup>	m. p. 110°-111°	NO <sup>2</sup>	—	NO <sup>2</sup>	—	Cl
Cl.NO <sup>2</sup> .NO <sup>2</sup>	80.5°	Cl	—	—	—	NO <sup>2</sup>
Br.NO <sup>2</sup> .NO <sup>2</sup>	117°	Br	—	NO <sup>2</sup>	—	NO <sup>2</sup>
Br.NO <sup>2</sup> .NO <sup>2</sup>	76°	NO <sup>2</sup>	—	Br	—	NO <sup>2</sup>
I.NO <sup>2</sup> .NO <sup>2</sup>	106°	I	—	NO <sup>2</sup>	—	NO <sup>2</sup>
I.NO <sup>2</sup> .NO <sup>2</sup>	113°	NO <sup>2</sup>	—	I	—	NO <sup>2</sup>
Cl.Cl.NO <sup>2</sup>	121°	Cl	—	Cl	—	NO <sup>2</sup>
Cl.Cl.NO <sup>2</sup>	125°	Cl	—	NO <sup>2</sup>	—	Cl
Br.Br.NO <sup>2</sup>	117.5°	Br	—	Br	—	NO <sup>2</sup>
Br.Br.NO <sup>2</sup>	141°	Br	—	NO <sup>2</sup>	—	Br
I.I.NO <sup>2</sup>	98°	I	—	I	—	NO <sup>2</sup>
I.I.NO <sup>2</sup>	157°	I	—	NO <sup>2</sup>	—	I
Br.SO <sup>2</sup> H.SO <sup>2</sup> H	From phenol- disulphonic acid	Br	—	SO <sup>2</sup> H	—	SO <sup>2</sup> H
Cl.Cl.SO <sup>2</sup> H	From dichlorophenol, 1 : 2 : 4	Cl	—	Cl	—	SO <sup>2</sup> H
Cl.Cl.SO <sup>2</sup> H	From phenolpara- sulphonic acid	Cl	—	SO <sup>2</sup> H	—	Cl

## Constitution of Phenol-derivatives.

Abbreviated symbol of compound	Description	Position of the displacing radicles relatively to the OH-group which occupies the position 1				
		Ortho, 2	Meta, 3	Para, 4	Meta, 5	Ortho, 6
Br.Br.SO <sup>3</sup> H	From phenolortho-sulphonic acid	Br	—	Br	—	SO <sup>3</sup> H
Br.Br.SO <sup>3</sup> H	From phenolpara-sulphonic acid	Br	—	SO <sup>3</sup> H	—	Br
I.I.SO <sup>3</sup> H	From phenolpara-sulphonic acid	I	—	SO <sup>3</sup> H	—	I
Cl.NO <sup>2</sup> .SO <sup>3</sup> H	From dichlorophenol-parasulphonic acid	Cl	—	SO <sup>3</sup> H	—	NO <sup>2</sup>
Cl.NO <sup>2</sup> .SO <sup>3</sup> H	From para-chlorophenolsulphonic acid	NO <sup>2</sup>	—	Cl	—	SO <sup>3</sup> H
Br.NO <sup>2</sup> .SO <sup>3</sup> H	From dibromophenol-parasulphonic acid	Br	—	SO <sup>3</sup> H	—	NO <sup>2</sup>
Br.NO <sup>2</sup> .SO <sup>3</sup> H	From parabromophenolsulphonic acid	NO <sup>2</sup>	—	Br	—	SO <sup>3</sup> H
Br.NO <sup>2</sup> .SO <sup>3</sup> H	From paranitrophenol-sulphonic acid	Br	—	NO <sup>2</sup>	—	SO <sup>3</sup> H
I.NO <sup>2</sup> .SO <sup>3</sup> H	From orthonitrophenol-parasulphonic acid	I	—	SO <sup>3</sup> H	—	NO <sup>2</sup>
I.NO <sup>2</sup> .SO <sup>3</sup> H	From paranitrophenol-sulphonic acid	I	—	NO <sup>2</sup>	—	SO <sup>3</sup> H

H. E. A.

**PHENOL, HOMOLOGUES OF.** The hydrocarbons homologous with benzene, which may be represented by the general formula,  $C^aH^{4-m}(C^bH^{2n+1})^m$ ,\* are capable of yielding two metameric series of monohydric alcohols; thus toluene,  $C^6H^4.CH^3$ , is convertible on the one hand into the cresols,  $C^6H^4(OH).CH^3$ , and on the other into benzyl alcohol,  $C^6H^5.CH^2(OH)$ , which is metameric with the cresols. The alcohols of the former class, which are termed *phenols*, on account of the resemblance they bear to phenol, the first term of the series, may be represented by the general expression,  $C^aH^{4-m}(OH)(C^bH^{2n+1})^m$ , the alcohols of the latter class, which for want of a better name may be termed *alcohols of the benzylic series*, being represented by the general formula,  $C^aH^{4-m} \left\{ \begin{matrix} C^bH^{2n}.OH \\ (C^bH^{2n+1})^m \end{matrix} \right.$ . In the case of the first term of the phenol series, the value of  $n$  and  $m$  in the general formula above given is zero, and the highest possible value of  $m$  is doubtless 5; the limits within which  $n$  may vary have not yet been determined, and cannot be predicted. In the alcohols of the benzylic series,  $m$  in the first term equals 0, and cannot exceed 5; the lowest value of  $n$ , however, in the  $C^aH^{2n}.OH$  group is 1. The limit of variation of  $n$  cannot be stated.

The following alcohols derived from hydrocarbons of the benzene series are known:—

Phenols, $C^aH^{4-m}(OH)(C^bH^{2n+1})^m$		b. p.	
$C^6H^4O$	Phenol or Oxybenzene	$C^6H^5.OH$	182
$C^6H^4O$	Paracresol or Paroxymethylbenzene	$C^6H^4.CH^3.OH$	200-205
	Metacresol or Metoxymethylbenzene		195-200
	Orthocresol or Orthoxymethylbenzene		185-186
$C^6H^4O$	Metaxyleneol (solid) or Oxymetadi-methylbenzene	$C^6H^3(OH) \left\{ \begin{matrix} CH^3 \\ CH^3 \end{matrix} \right.$	216
	Xyleneol (liquid) or Oxydimethylbenzene		212
$C^6H^4O$	Ethylphenol (solid) or Paroxyethylbenzene		214-216
	Ethylphenol (liquid) or Orthoxyethylbenzene	$C^6H^4.C^2H^5.OH$	212
	Phlorol (?) Oxyethylbenzene		220
	(Thymol; $\alpha$ -Cymophenol or Oxypara-methylpropylbenzene		230
$C^{10}H^{14}O$	Carvacrol; $\beta$ -Cymophenol or Oxy-paramethylpropylbenzene	$C^8H^7(OH) \left\{ \begin{matrix} CH^3 \\ C^2H^5 \end{matrix} \right.$	233

\* The value of  $m$  may be 0 and cannot exceed 5; when there are several  $C^bH^{2n+1}$  groups in the hydrocarbon, the value of  $n$  may be the same or different in each of these.

Alcohols of the Benzyllic series,  $C^aH^{a-n}\{C^aH^{a-n}OH\}_n$

			b. p.
$C^aH^aO$	Benzyl alcohol . . . . .	$C^aH^a.OH^2(OH)$ . . . . .	207
$C^aH^{a-1}O$	{ Paratolyl alcohol . . . . .	$C^aH^a(CH^3).CH^2(OH)$ . . . . .	217
	{ Secondary Phenylethyl alcohol . . . . .	$C^aH^a.CH(OH).CH^3$ . . . . .	203
$C^aH^{a-2}O$	{ Primary Phenylpropyl alcohol . . . . .	$C^aH^a.CH^2.CH^2.OH^2(OH)$ . . . . .	235
	{ Secondary Phenylpropyl alcohol . . . . .	$C^aH^a.CH(OH).CH^2.CH^3$ . . . . .	211
$C^aH^{a-1}O$	{ Caminyl alcohol . . . . .	$C^aH^a(CH^3).CH^2(OH)$ . . . . .	243
	{ Secondary Phenylbutyl alcohol . . . . .	$C^aH^a.CH(OH).CH^2.CH^2.CH^3$ . . . . .	—
$C^{10}H^{10}O$	Sycoceryl alcohol . . . . .		—

PARACRESOL,  $C^aH^aO = C^aH^a(CH^3).OH$  (1 : 4). All the specimens of commercial cresol or cresylic acid (from coal-tar) hitherto examined have been found to contain more or less of this cresol; it is impossible to separate it in a pure state, however, by any of the ordinary processes, such as fractional solution in alkali, fractional precipitation from an alkaline solution, or fractional distillation (Armstrong). Its presence in the coal-tar product was first demonstrated by H. Buff (*Deut. Chem. Ges. Ber.* 1871, 378), who on treating the portion boiling constantly at  $204^\circ$ – $205^\circ$  with benzoic chloride, obtained a mixture of crystalline benzoylparacresol with a liquid substance (probably benzoylorthocresol). The cresol separated from the benzoyl derivative melted at  $34^\circ$ , and boiled at about  $205^\circ$ .

Pure paracresol may also be prepared from crude coal-tar cresol by heating this liquid with an equal weight of concentrated sulphuric acid for about 15 hours to  $100^\circ$ . The resulting mixture of sulpho-acids is dissolved in water and neutralised with barium carbonate; a concentrated hot solution of barium hydrate is then added to the warm filtered solution until no further precipitate is formed. The precipitate of basic barium paracresolsulphonate thus obtained is separated from the liquid, decomposed by the necessary quantity of diluted sulphuric acid, the solution is neutralised with potassium carbonate, and allowed to crystallise; the resulting potassium paracresol-sulphonate is purified by recrystallisation, and then heated in sealed tubes with hydrochloric acid for 2–3 hours to  $140^\circ$ – $150^\circ$ , whereby it is resolved into paracresol and potassium-hydrogen sulphate. It is advantageous first to distil the cresol in a current of steam before distilling it alone (Armstrong a. Field, *Chem. News*, xxix. 282).

Southworth (*Ann. Ch. Pharm.* clxviii. 267) finds that pure paracresol is not converted into chlorinated quinones (1st *Suppl.* 507) when it is submitted to the action of hydrochloric acid and potassium chlorate, but that it yields a dark-coloured uncrystalline product which he regards as being probably a mixture of chlorocresols. The chlorinated quinones obtained by Graebe a. Borgmann from coal-tar cresol were in all probability orthocresol derivatives.

**Nitroparacresols**,  $C^aH^a.CH^3.NO^2.OH$ .—When nitric acid (1 mol.) is gradually added to a cold glacial acetic acid solution of paracresol (1 mol.), and the mixture then poured into water, a black oil is obtained, which on distillation in a current of steam furnishes nitroparacresol as a yellow oil. The resinous residue in the flask yields, on extraction with boiling water, a small quantity of a substance which crystallises in white, diffu- cultly soluble needles, melting at  $126^\circ$ – $127^\circ$ ; this is probably an isomeric nitroparacresol. The yellow oil solidifies when cooled by ice, and the solid may be purified by cresol. The yellow oil solidifies when cooled by ice, and the solid may be purified by recrystallisation from alcohol (Armstrong). This nitroparacresol is identical with that which Wagner obtained (*Deut. Chem. Ges. Ber.* vii. 537, 1269), by heating ortho- nitroacetoparatoluidine with sodium hydrate. Orthonitroparacresol ( $OH : NO^2 : CH^3 = 1 : 2 : 4$ ) is scarcely soluble in water but very soluble in alcohol and ether, from which it crystallises in yellow flattened needles; it melts at  $33^\circ$ – $33.5^\circ$ . It possesses the peculiar odour of volatile nitrophenol. Orthonitroparacresol has extremely feeble acid properties, and its metallic derivatives are difficult to prepare, on account of their instability, being decomposed when boiled with water. The *potassium and sodium derivatives* form dark red needles easily soluble in water and alcohol; the *silver derivative* separates, on addition of silver nitrate to a solution of the sodium derivative, as a brick-red precipitate. The *lead derivative* forms an orange-yellow very difficultly soluble precipitate. The *barium derivative* crystallises from the concentrated solution in pale-red crystalline scales. The *methyl derivative*,  $C^aH^a.CH^3.NO^2.OCH^3$ , which is obtained by acting on the silver derivative with methyl iodide, is a yellow oil, boiling with partial decomposition at  $274^\circ$ ; during the formation of this compound, much metallic silver separates. It is converted by heating with alcoholic ammonia at  $160^\circ$ – $180^\circ$  into orthonitroparatoluidine (m. p.  $168^\circ$ ) identical with that from which it may be produced by boiling with solution of sodium hydrate (Wagner).

Orthonitroparacresol is readily converted by nitric acid into dinitroparacresol (m. p. 84°); the (probably) isomeric nitroparacresol yields a different substance (Armstrong).

*Orthoamidoparacresol*,  $C^6H^3.CH^3.NH^2.OH$  (Wagner, *Deut. Chem. Ges. Ber.* vii. 1270), is prepared by reducing orthonitroparacresol (m. p. 33°) with tin and hydrochloric acid; it is separated from the hydrochloride by ammonia and recrystallised from boiling water, and is thus obtained in white glistening scales almost insoluble in cold water, but easily soluble in alcohol and ether. It separates from the solution in ether in large rhombic crystals. The *hydrochloride* forms long white needles, easily soluble in water and alcohol, difficultly soluble in ether. A platinum double salt could not be obtained.

Orthoamidoparacresol hydrochloride is converted into orthodiazoparacresol hydrochloride by ethyl nitrite, but on account of its easy solubility the diazo-compound is difficult to isolate. It yields with platinum chloride a double salt,  $C^6H^3.ON^2.Cl.FtCl^4$ , resembling ammonium-platinum chloride in appearance (Wagner). On dry distillation this double salt furnishes a chlorocresol.

*Dinitroparacresol*,  $C^6H^3.CH^3.(NO^2)^2.OH$  (?  $OH : NO^2 : CH^3 : NO^2 = 1 : 2 : 4 : 6$ ).—This compound, which may be obtained by the action of nitrous acid on paratoluidine (1st Suppl. 508) is also produced—1. By nitration of orthonitroparacresol (Armstrong a. Field).—2. By nitration of potassium paracresolorthosulphonate (Armstrong a. Field; Pechmann, *Ann. Ch. Pharm.* clxxiii. 205).—3. By heating dinitroparacetotoluidine with sodium hydrate solution (Wagner). It crystallises in lemon-yellow needles, melting at 84°, slightly soluble in water, very soluble in alcohol and ether. When treated with even the strongest nitric acid, it does not yield a trinitro-derivative (Armstrong, *Deut. Chem. Ges. Ber.* vii. 406).

*Potassium dinitroparacresol*,  $C^6H^3.(NO^2)^2.OK$ , crystallises in long carmine-red flattened needles, easily soluble in hot, but much less soluble in cold water. The *ammonium derivative* forms anhydrous red needles. The *barium derivative*,  $[C^6H^3.(NO^2)^2.O]^2Ba$ , separates in fine yellow difficultly soluble needles. The *lead derivative* also forms fine yellow anhydrous needles. The *silver derivative*,  $C^6H^3.(NO^2)^2.OAg$ , crystallises in beautiful carmine-red needles (Pechmann).

*Paracresolorthosulphonic acid*,  $C^6H^3.CH^3.OH.SO^3H$  ( $OH : SO^3H : CH^3 = 1 : 2 : 4$ ). Pechmann's *Paracresolmetasulphonic acid*,  $CH^3 : SO^3H : OH = 1 : 3 : 4$ . *Paracresolsulphuric acid* (1st Suppl. 566).—According to Barth (*Ann. Chem. Pharm.* cliv. 384), and Biedermann (*Deut. Chem. Ges. Ber.* vi. 326), protocatechuic acid,  $C^6H^4(OH)^2.CO^2H$ , is formed when potassium paracresolsulphonate from paracresol is fused with potassium hydrate; Pechmann (*Ann. Ch. Pharm.* clxxiii. 204) using that prepared from paratoluidinemetasulphonic acid ( $OH^2 : SO^3H : NH^2 = 1 : 3 : 4$ ) obtained chiefly paroxybenzoic acid, and only traces of protocatechuic acid.

The action of bromine on potassium paracresolorthosulphonate gives rise to the formation, first of bromo- then of dibromoparacresolsulphonate, which, by the continued action of the bromine, appears to be converted into tribromoparacresol. The dibromosulpho-salt is the main product, however, even when only 1 mol. of bromine is added to 1 mol. of the salt (Armstrong a. Field). Dilute nitric acid converts potassium paracresolorthosulphonate into nitroparacresolorthosulphonate, which, by the continued action of the acid, yields dinitroparacresol (m. p. 84°) (Armstrong a. Field). Little, however, is at present known of these derivatives.

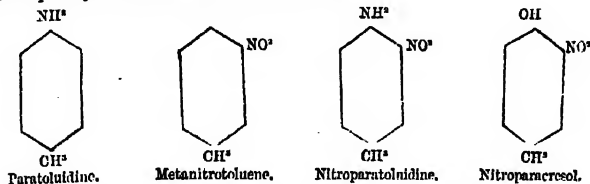
*Paracresolmetasulphonic acid*,  $C^6H^3.CH^3.OH.SO^3H$  ( $OH : SO^3H : CH^3 = 1 : 3 : 4$ ). Jensen's *Paracresolorthosulphonic acid*, ( $CH^3 : SO^3H : OH = 1 : 2 : 4$ ).—This acid is produced by heating the diazo-derivative of paramidotolueneorthosulphonic acid ( $CH^3 : SO^3H : NH^2 = 1 : 3 : 4$ ) from paranitrotoluene and sulphuric acid with water (Jensen, *Ann. Chem. Pharm.* clxxii. 230). It crystallises from water in long white needles with 5 mols. of water, which melt at 98.5°; on exposure over sulphuric acid they lose the water of crystallisation and then melt at 187°–168°. All the salts of this acid are very soluble and could not be obtained in a crystalline state; the barium salt is not precipitated by barium hydrate.

A nitroparacresolmetasulphonic acid is produced when the nitrodiazo-acid formed by the action of fuming nitric acid on paramidotolueneorthosulphonic acid is heated with water. An orthobromoparacresolmetasulphonic acid may be similarly prepared from metabromoparamidotolueneorthosulphonic acid (Weckwarth, *Ann. Chem. Pharm.* clxxii. 201).

*Chlorocresol*,  $C^6H^3.Cl.CH^3.OH$ .—By passing chlorine into heated cresol (from coal-tar) and fractionally distilling the product, Biedermann (*Deut. Chem. Ges. Ber.* vi. 326) obtained a chlorocresol crystallising in long needles, which melt at 66°, and boil without decomposition at about 240°. The cresol employed evidently contained a considerable proportion of paracresol, so that this chlorocresol may be a paracresol derivative.

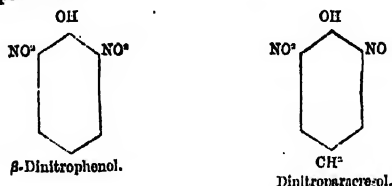
By the action of iodine and iodic acid in an alkaline solution on the same cresol in the proportions required to form an iodocresol, Biedermann obtained an oily product, which he decomposed with alcoholic potassium hydrate at 250°-300°. The product was an amorphous yellowish-red substance, which, on analysis, gave numbers agreeing approximately with those required by the formula  $\text{C}^6\text{H}^3\text{CH}^2\text{OH}\{\text{O}\}$ .

*Constitution of the Paracresol derivatives.*—The constitution of the volatile nitro-paracresol is given by its formation from nitroparatoluidine. Thus Bülstein & Kuhlberg have shown (*Ann. Chem. Pharm.* clv. 1) that the nitroparatoluidine procurable from aceto-paratoluidine by nitration, &c., yields, on removal of the amido-group, a metanitrotoluene (1 : 3), which enables us to infer the constitution of nitrotoluidine, and consequently of nitroparacresol, to be as follows :

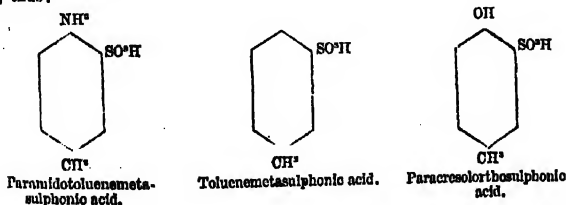


The very great resemblance which nitroparacresol bears to the volatile orthonitrophenol serves to confirm this conclusion that the nitro-group is in the ortho-position.

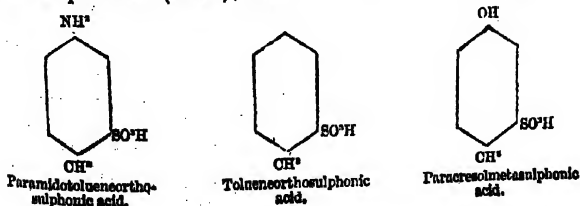
In dinitroparacresol (m. p. 84°) the nitro-groups probably occupy the ortho-positions : firstly, because of the close resemblance which it bears to  $\beta$ -dinitrophenol ; and secondly, because, as previously pointed out, in the case of nearly all phenol derivatives directly prepared from phenol, the para- and ortho-positions are occupied, and not the meta-positions :



The cresolsulphonic formed directly from paracresol has the sulpho-group in the ortho-position. This is shown by its formation from paramidotoluenemetasulphonic acid, which, on removal of the  $\text{NH}^2$  group, yields toluenemetasulphonic acid (Pechmann) ; thus :



In a similar manner the isomeric acid is shown to have the sulpho-group in the meta-position, by its formation from an amidotoluenesulphonic acid which yields tolueneorthosulphonic acid (Jensen) ; thus :



**METACRESOL**,  $C^6H^4.O = C^6H^4.CH^3.OH$  (1 : 3).—Southworth (*Ann. Chem. Pharm.* clxviii. 267) recommends the use of 50 grams of phosphoric anhydride in place of the 35 grams employed by Engelhardt a. Latschinoff (*1st Suppl.* 507) to decompose 100 grams of thymol. By the action of potassium chlorate and hydrochloric acid, meta-cresol is converted into *dichlorotoluenetaquinone*,  $C^6H^2.Cl^2O^2$  (Southworth).

**Metaresolsulphonic acid**,  $C^6H^4.CH^3.OH.SO^3H$ .—When the metabromotolueneortho-sulphonic acid, prepared by Griess's method from the metabromoparamidotoluene-orthosulphonic acid formed on adding bromine to a solution of paramidotolueneortho-sulphonic acid, is treated with moist silver oxide, the bromine is displaced by OH, and a metaresolsulphonic acid produced, the potassium salt of which crystallises in beautiful coarse needles. Orthobromotoluenemetasulphonic acid is similarly acted upon (Weekwarth, *Ann. Chem. Pharm.* clxxii. 201).

**ORTHO-CRESOL**,  $C^6H^4.O = C^6H^4.CH^3.OH$  (1 : 2).—Kekulé (*Dent. Chem. Ges. Ber.* vii. 1006) has obtained pure orthocresol by heating carvacrol, the isomeride of thymol, with phosphoric anhydride, and fusing the resulting cresyl phosphate with potassium hydrate; and by Griess's method from orthotoluidino. It melts at  $31^{\circ}$ – $31^{\circ}5'$ , and boils at  $185^{\circ}$ – $186^{\circ}$ . The benzoyl-derivative remains liquid even when very strongly cooled. Orthocresotol, from pure orthocresol, melts at  $163^{\circ}$ – $164^{\circ}$ , and not, as stated by Engelhardt a. Latschinoff (*1st Suppl.* 508), at  $114^{\circ}$ .

The cresol obtained by Körner (*1st Suppl.* 507) from bromophenol appears to have been meta-cresol (1 : 3). Henry's dichlorocresol (*ibid.*), from salicylic aldehyde, is an orthocresol (1 : 2) derivative.

Commercial cresol, from coal-tar, appears always to contain paracresol and orthocresol in varying proportions mixed with more or less phenol (Armstrong a. Field).

**Orthocresolparasulphonic acid**,  $C^6H^4.CH^3.OH.SO^3H$  (OH :  $CH^3$  :  $SO^3H$  = 1 : 2 : 4), is produced on heating orthodiazotolueneparasulphonic acid with water, and, but in a much purer form, by adding the diazo-compound to gently warmed fuming sulphuric acid (Hayduck, *Ann. Chem. Pharm.* clxxii. 204; clxxiv. 343). The *barium salt*,  $(C^6H^4.OH.SO^3)^2Ba + 1\frac{1}{2}H^2O$ , is extremely soluble; it crystallises in aggregates which, under the microscope, are seen to consist of monoclinic prisms. The *potassium salt*,  $C^6H^4.OH.SO^3K + \frac{1}{2}H^2O$ , dissolves in water in all proportions, and is also very easily soluble in alcohol; from a saturated solution in anhydrous alcohol it separates as a yellowish crystalline powder, and from an aqueous alcoholic solution, on slow evaporation, in groups of short needles. It yields salicylic acid when fused with potassium hydrate.

**Ethylorthocresolparasulphonic acid**,  $C^6H^4.CH^3.OC^2H^5.SO^3H$ , is formed when orthodiazotolueneparasulphonic acid is boiled with absolute alcohol. The *potassium salt*,  $C^6H^4.(OC^2H^5)SO^3K + H^2O$ , crystallises in glistening white needles united in lamellae; it is very soluble in water. The *barium salt*,  $[C^6H^4.(OC^2H^5)SO^3]^2Ba + 3H^2O$ , separates from concentrated solutions in aggregates of microscopic needles, and from less concentrated solutions in needles; it is somewhat difficultly soluble in cold, but easily soluble in hot water. The *lead salt*,  $[C^6H^4.(OC^2H^5)SO^3]^2Pb + 3H^2O$ , forms long hair-fine white glistening needles, united in groups; it is easily soluble in hot water. The *chloride*,  $C^6H^4.(OC^2H^5)SO^3Cl$ , prepared from the potassium salt and phosphorus pentachloride, is a yellowish oil, from which rhombic plates separate on standing over sulphuric acid; ammonia converts it into the *amide*,  $C^6H^4.(OC^2H^5)SO^3NH^2$ , which crystallises in glistening plates melting at  $137^{\circ}$ , difficultly soluble in hot water (Hayduck).

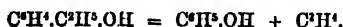
**Methylorthocresolparasulphonic acid**,  $C^6H^4.CH^3.OCH^3.SO^3H$ , is similarly prepared with the aid of methyl alcohol. The *barium salt*,  $[C^6H^4.(OCH^3)SO^3]^2Ba + 2H^2O$ , crystallises in small glistening plates, somewhat more soluble in water than the ethyl compound (Hayduck).

**Nitroorthocresolparasulphonic acid**,  $C^6H^4.CH^3.NO^2.OH.SO^3H$ , is obtained by heating nitroorthodiazotolueneparasulphonic acid with water or sulphuric acid. The *barium salt*,  $[C^6H^4.(NO^2)OHSO^3]^2Ba + 5H^2O$ , crystallises in hard yellow monoclinic prisms of considerable size; it is easily soluble in water. The *dibarium salt*,  $[C^6H^4.(NO^2)SO^3]^2Ba^2 + 6\frac{1}{2}OH^2$ , forms tufts of orange-red needles, easily soluble in hot water (Hayduck).

**Dibromorthocresolparasulphonic acid**,  $C^6H^4.Br^2.OH.SO^3H$ .—This acid is obtained by heating dibromorthodiazotoluene-sulphonic acid, prepared from the dibromo-acid formed from bromine and orthamidotoluene-sulphonic acid, with water. The *barium salt*,  $[C^6H^4.Br^2OHSO^3]^2Ba + 8\frac{1}{2}H^2O$ , forms easily soluble glistening plates. The *potassium salt*,  $C^6H^4.Br^2OHSO^3K + H^2O$ , crystallises similarly (Hayduck).

**XYLENOLS**,  $C^6H^{10}O = C^6H^4(CH^3)_2OH$  (see 1st Suppl. 1128).

**ETHYLPHENOLS**,  $C^6H^{10}O = C^6H^4.C^2H^5.OH$ .—The crystalline ethylphenol obtained by Fittig & Kiesow and by Beilstein & Kuhlberg (*ibid.* 916 \*) on fusing potassium ethylbenzenesulphonate,  $C^6H^4.C^2H^5.SO^3K$ , with potassium hydrate, in oil probably corresponds with paraeresol, and the liquid phenol with orthoeresol. When heated with phosphoric anhydride, solid ethylphenol is converted into a phenylphosphate and ethylene is evolved (Chrutschoff, *Deut. Chem. Ges. Ber.* v.i. 1165):



**PHLOROL**, **PHLORETOL**,  $C^6H^{10}O = (?)C^6H^4.C^2H^5.OH$  (v. 493; 1st Suppl. 928).—Körner & Corbetta (*Deut. Chem. Ges. Ber.* vii. 1731) have recently shown that when methylphloreotic acid is oxidised it is converted into anisic acid, thus proving phloreotic acid to be a phenolpropionic acid,  $C^6H^4(OH).C^2H^4.COOH$ . Since phlorol is obtained on distilling barium phlorotate with caustic lime, this observation appears to prove that phlorol is an ethylphenol in which the ethyl and OH-group occupy the positions 1 : 4; phlorol, however, according to Hlasiwetz's description, has very different properties from those of crystalline ethylphenol, which, there is much reason to believe, is a para-derivative.

**THYMOL**,  **$\alpha$ -CYMOPHENOL**, **OXYPARAMETHYLPROPYLBENZENE**,  $C^6H^{14}O = C^6H^4.OH \left\{ \begin{smallmatrix} C^3H^7 \\ CH^3 \end{smallmatrix} \right\}$  ( $OH : CH^3 : C^3H^7 = 1 : 3 : 6$ ).—According to Carstanjen (*J. pr. Chem.* [2], iii. 53) the thymoöl which Lallemand prepared by oxidising thymolsulphonic acid with manganic peroxide and sulphuric acid (v. 792), and to which he gave the formula  $C^{12}H^{16}O^2$ , is in reality thymoquinone,  $C^{10}H^{12}O^2$ , which on reduction yields Lallemand's thymoöl or thymohydroquinone,  $C^{10}H^{12}(OH)^2$ . The diamidothymol obtained from dinitrothymol (v. 795) yields oxythymoquinone,  $C^{10}H^{14}(OH)O^2$ , on oxidation. When thymol is distilled with phosphorus pentachloride, a chlorocymene,  $C^{10}H^{14}Cl$ , is produced, which, on reduction with sodium amalgam, yields cymene,  $C^{10}H^{14}$  (b. p. 174°–176°); this cymene is converted, on oxidation, into terephthalic acid (Carstanjen). When thymol is distilled with phosphorus pentasulphide, it furnishes cymene identical with camphor-cymene and the mercaptan,  $C^{10}H^{12}.SH$  ( $\alpha$ -thiocymene), corresponding with thymol (Fittica, *Deut. Chem. Ges. Ber.* vi. 938; *Ann. Chem. Pharm.* clxii. 303).

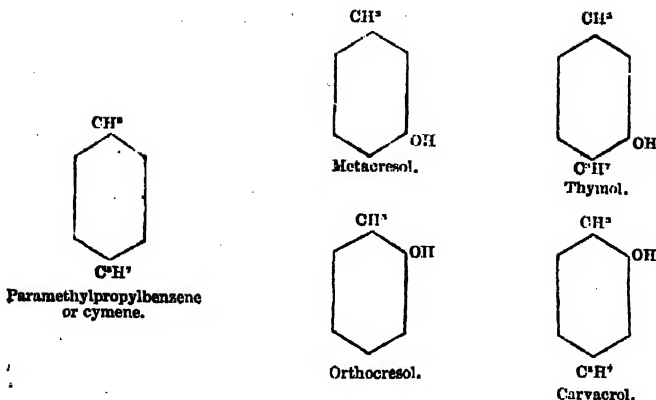
**CARVACROL**,  **$\beta$ -CYMOPHENOL**, **OXYPARAMETHYLPROPYLBENZENE**,  $C^6H^{14}O = C^6H^4.OH \left\{ \begin{smallmatrix} C^3H^7 \\ CH^3 \end{smallmatrix} \right\}$  ( $OH : CH^3 : C^3H^7 = 1 : 2 : 5$ ).—When carvol (i. 808) is warmed with a small quantity of orthophosphoric acid, much heat is evolved, and it is converted into carvacrol (Kekulé & Fleischer, *Deut. Chem. Ges. Ber.* vi. 1087). Carvacrol is also produced when camphor is heated for some time with  $\frac{1}{2}$  of its weight of iodine (*ibid.* 934). The compound thus obtained from carvol and camphor is identical with Post & Müller's cymophenol, formed on fusing the potassium salt of cymene-sulphonic acid (from camphor-cymene) with potassium hydrate (1st Suppl. 1089).

Carvacrol boils at 232°–232.5° (at 236°–237° when the entire mercury column of the thermometer is immersed in the vapour); when distilled with phosphorus trisulphide or pentasulphide it yields cymene and  $\beta$ -thiocymene, more of the latter being obtained if the pentasulphide be employed. The thiocymene is isomeric with that formed from thymol. When carvacrol is heated with phosphoric anhydride, propylene is evolved; the residue yields orthoeresol when decomposed with potassium hydrate, &c. Phosphorus pentachloride converts it into chlorocymene, boiling at 214°.

Carvacrolsulphonic acid is crystalline and yields crystalline salts; when oxidised by manganic oxide and sulphuric acid, it furnishes thymoquinone identical with that obtained from thymol. The acid,  $C^6H^4.CH^3.C^3H^7.OH.CO^2H$ , produced on treating carvacrol with sodium and carbonic anhydride, melts at 133°–134°, the isomeric acid from thymol melting at 120°.

*Constitution of the Cymophenols*.—Thymol and carvacrol are both derived from the same methylpropylbenzene or cymene. This is proved by the conversion of thymol by the action of phosphorus pentasulphide into cymene identical with that contained in Ptychotis oil, and which can be produced by heating camphor with phosphorus pentasulphide or pentoxide, from which Müller & Post respectively obtained carvacrol. This methylpropylbenzene is shown to contain methyl and normal propyl in the para-position, by its formation from crystalline bromotoluene, normal propyl bromide and sodium (Fittica). Finally, the position of the OH-group is determined by the conversion of thymol into metaeresol, and of carvacrol into orthoeresol; thus:

\* The name *phenetol*, and the formula  $C^6H^4.(C^2H^5)_2O$ , is there wrongly assigned to this compound.



**BENZYL ALCOHOL**,  $C^6H^5O = C^6H^5.CH^2(OH)$ .—See vol. i. p. 578, and 1st *Suppl.* 334; also p. 177 of this volume.

**PARATOLYL ALCOHOL**,  $C^6H^5O = C^6H^4(CH^3)CH^2(OH)$ .—This alcohol, which is described in vol. v. p. 869, has the methyl and  $CH^2(OH)$ -group in the para-position, since it is obtained by the action of nascent hydrogen on the aldehyde of ordinary *p*-*paratoluic acid*,  $C^6H^4.CH^3.COOH$  ( $CH^3 : COOH = 1 : 4$ ).

**SECONDARY PHENYLETHYL ALCOHOL**,  $C^6H^5O = C^6H^4.CH(OH).CH^3$ .—This alcohol is produced by the action of sodium-amalgam on a dilute alcoholic solution of acetophenone,  $C^6H^5.CO.CH^3$ , together with the corresponding pinacone (Emmerling a. Engler, *Deut. Chem. Ges. Ber.* vi. 1005); and by saponification of the acetate formed by the action of bromethylbenzene,  $C^6H^5.CHBr.CH^3$ , on silver acetate (Radziszewski, *ibid.* vii. 140). It is a colourless, highly refractive liquid, possessing an extremely unpleasant odour. It boils at  $202^\circ$ – $203^\circ$ . By the action of hydrobromic acid it is converted into bromethylbenzene; and by the action of hydrochloric acid into chlorethylbenzene boiling at about  $194^\circ$ . The properties of the chlorethylbenzene thus obtained agree fairly with the description given by Fittig of the chlorethylbenzene formed by chlorinating ethylbenzene, but since the latter furnishes hydrocinnamic acid when the chlorine is replaced by carboxyl (1st *Suppl.* 469), the two compounds must be isomeric (Emmerling a. Engler).

**PRIMARY PHENYLPROPYL ALCOHOL**,  $C^6H^5O = C^6H^4.CH^2.CH^2(OH)$ .—This alcohol is present in storax, probably as cinnamic ether, and is contained in considerable quantity in commercial cinnamic alcohol. It may be produced by the action of nascent hydrogen on cinnamic alcohol (Fittig, *Deut. Chem. Ges. Ber.* vi. 215). It is a colourless thick liquid, of sp. gr. 1.008 at  $18^\circ$ , which boils at  $235^\circ$ ; on oxidation it yields hydrocinnamic acid.

*Phenylpropyl acetate*,  $C^6H^5.O.C^6H^5O$ , is a yellowish, almost odourless liquid, much more mobile than the alcohol; it boils at  $244^\circ$ – $245^\circ$ . Like the alcohol it does not solidify at  $-18^\circ$ .

**SECONDARY PHENYLPROPYL ALCOHOL**,  $C^6H^5O = C^6H^4.CH(OH).CH^2.CH^3$ .—This alcohol is formed by the action of sodium-amalgam on a dilute alcoholic solution of propiophenone,  $C^6H^5.CO.OH^2.CH^3$ . It boils at  $210^\circ$ – $211^\circ$ , but is partially decomposed (Barry, *Deut. Chem. Ges. Ber.* vi. 1008).

**CUMIC or CUMINYL ALCOHOL**,  $C^6H^5O = C^6H^4.C^6H^4.OH^2(OH)$ .—See vol. ii. p. 298. The propyl and  $OH^2(OH)$ -group in this alcohol are in the para-position, since it ultimately furnishes terephthalic acid on oxidation.

**SECONDARY PHENYLBUTYL ALCOHOL**,  $C^6H^5.CH(OH).CH^2.CH^2.CH^3$ , is produced by the action of nascent hydrogen on phenylpropyl ketone, but has not yet been examined (*Deut. Chem. Ges. Ber.* vii. 1128).

**SYCOBENNYLIC ALCOHOL**,  $C^6H^5O$ . See vol. v. p. 845.

H. E. A.



**PHENOQUINONE**,  $C^{12}H^{10}O^4$  (see QUINONES).

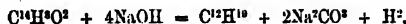
**PHENYL (DI-)**,  $C^{12}H^{10}$ . *Formation*.—1. By heating potassium phenate with potassium benzoate (Pfankuch, *J. pr. Chem.* [2], i. 451):—



2. By heating potassium phenate with oxalate (Pfankuch, *ibid.* iv. 35).

3. Together with anilino, acetone, and a small quantity of diphenylamine, by heating sodium phenate with acetanilide (Weith, *Deut. Chem. Ges. Ber.* vi. 966).

4. By heating phenanthrene-quinone with soda-lime (Graebe, *Ann. Ch. Pharm.* clxvii. 181):



*Preparation*.—Engelhardt a. Latschinoff (*Zeitschr. f. Chem.* [2], vii. 259) prepare this compound by mixing 780 grams of benzene with 25 grams of iodine and 1.256 grams of bromine. The reaction goes on quietly, but towards the end the heat of the water-bath has to be applied. On distillation, the portion boiling below  $159^\circ$  is collected separately, and, after drying and removing all traces of hydrobromic acid, 150 grams of sodium are added. If the reaction does not begin by itself, it is started by gentle heating, but as soon as it begins the mixture must be well cooled. The products consist of excess of benzene, diphenyl (of which 120 grams were obtained), and a liquid having a very high boiling point. In the retort there remains, besides sodium iodide, a black solid which can be volatilised by very strong heat.

*Reactions*.—Diphenyl is not altered by passing through a red-hot tube 3 feet long, filled with fragments of pumice (Dreher a. Otto, *Ann. Ch. Pharm.* cliv. 93).

By a solution of *chromic oxychloride* in glacial acetic acid, it is oxidised to benzoic acid (Carstanjen, *J. pr. Chem.* [2], i. 79).

With *formaldehyde* it produces a hydrocarbon which separates from chloroform in small crystals (Bayer, *Deut. Chem. Ges. Ber.* vi. 220).

**Bromodiphenyl**,  $C^{12}H^8Br$  or  $C^6H^5.C^6H^4Br$ , is formed by adding bromine to a solution of diphenyl in carbon sulphide. It crystallises in laminae melting at  $89^\circ$  and boiling at  $310^\circ$ , and yields by oxidation parabromobenzoic acid, which is also formed by the oxidation of dibromodiphenyl (Engelhardt a. Latschinoff).

**Chlorodiphenyl**,  $C^{12}H^8Cl$  =  $C^6H^5.C^6H^4Cl$ , is formed by distilling diphenyl-phenol with phosphorus pentachloride. It melts at  $75^\circ$ , and is converted by oxidation into parabromobenzoic acid (G. Schultz, *Deut. Chem. Ges. Ber.* vii. 52).

**Nitro-**, and **Amido-diphenyls** (Schultz, *loc. cit.*; Osten, *Deut. Chem. Ges. Ber.* vii. 170). **Mononitrodiphenyl**,  $C^{12}H^9NO^2$  =  $C^6H^5.C^6H^4NO^2$ , is obtained by treating diphenyl with excess of strong nitric acid in the cold, or with the required quantity in a hot acetic acid solution (Schultz), or by adding 4 pts. of fuming nitric acid diluted with 44 pts. of glacial acetic acid to 40 pts. of acetic acid in which are suspended 5 pts. of diphenyl; the latter then dissolves, and after a short time crystals of nitrodiphenyl make their appearance (Osten). It is also produced by converting amidonitrophenyl into a diazo-compound, and boiling the latter with alcohol (Schultz).

Mononitrodiphenyl crystallises in long colourless needles, which are insoluble in water, easily soluble in chloroform, ether, and hot alcohol. It melts at  $113^\circ$ , volatilises at a high temperature, and boils at  $340^\circ$ .

**Monamidodiphenyl**,  $C^{12}H^9NH^2$ .—The hydrochloride of this base is produced by treating nitrodiphenyl with tin and hydrochloric acid; the tin is then removed by sulphuretted hydrogen, and after rendering the solution alkaline with sodium hydrate, the liberated base may be at once collected on a filter or distilled in a current of steam. It crystallises from dilute alcohol in thin glistening scales, which melt at  $48^\circ$ – $49^\circ$  (Osten), at  $49^\circ$ – $50^\circ$  (Schultz), and are readily soluble in alcohol. The *hydrochloride*,  $C^{12}H^9NH^2.HCl$ , crystallises in colourless scales which are soluble in water. The *sulphate*,  $(C^{12}H^9NH^2)^2H^2SO^4$ , likewise forms colourless scales which dissolve with difficulty in cold, more readily in hot water. The *oxalate*,  $(C^{12}H^9NH^2)^2H^2CO^4$ , crystallises in long white needles which are soluble in water and in alcohol. The *nitrate*,  $C^{12}H^9NH^2.HNO^3$ , forms iridescent scales soluble in water. The *platinohydrochloride*,  $2(C^{12}H^9NH^2.HCl).PtCl^4 + 2H^2O$ , forms yellow glistening scales, moderately soluble in hot alcohol.

The properties of the base and of its salts show that it is identical with Hofmann's xenyamine (v. 1054).

**Acetamidodiphenyl**,  $C^{12}H^9.C^6H^4.NH.COCH^3$ , prepared by the action of glacial acetic acid on amidodiphenyl, forms long colourless needles which melt at  $187^\circ$  and dissolve easily in alcohol (Osten).

**Dinitrodiphenyl**,  $C^{12}H^8(NO^2)^2$  (iv. 410), is not oxidised by heating it with acetic acid and chromic trioxide, but *amidonitrodiphenyl*,  $C^{12}H^9(NO^2)(NH^2)$ , is thereby

converted into *paranitrobenzoic acid*. When this amido-compound is converted into *bromonitrodiphenyl* by means of the diazo-reaction, and the latter is oxidised, it yields *paranitro- and parabromobenzoic acid*. The same *bromonitrodiphenyl* is obtained, together with another compound, probably an isomeride, by nitrating *monobromodiphenyl*; it is almost insoluble in cold alcohol, sparingly in hot alcohol, and crystallises from toluene in colourless needles melting at  $173^{\circ}$  and boiling above  $360^{\circ}$ . From this it appears that *dinitrodiphenyl* is a *dipara-compound*, and this is further proved by the fact that by converting *benzidine* into *dibromodiphenyl*, a compound is obtained which is identical with common *dibromodiphenyl*, both yielding by oxidation *parabromobenzoic acid*. When *Fittig's isodinitrodiphenyl* (iv. 410) is reduced with hydrogen sulphide, *isocamiditrodiphenyl* is produced, crystallising from alcohol in short red prisms which melt at  $92^{\circ}$ - $93^{\circ}$ . It differs from the *para-compound* by forming crystallisable salts. The *hydrochloride*,  $C^{12}H^{10}(NO^2)(NH^2).HCl$ , crystallises in long white needles which may be dried at  $100^{\circ}$ , and decompose only when washed with a large quantity of water (Schultz).

*Tetranitrodiphenyl*,  $C^{12}H^4(NO^2)^4$ , is formed by dissolving *dinitrodiphenyl* in fuming nitric acid, or by acting on *diphenyl* with a large excess of a mixture of equal volumes of strong nitric and sulphuric acids. On adding water to the solution the *tetranitrodiphenyl* separates as an amorphous mass, which dissolves sparingly in alcohol and more readily in ether, from which solvent it separates as a friable amorphous mass melting at  $140^{\circ}$ . By ammonium sulphide, or by tin and hydrochloric acid, it is reduced to a mixture of amido-compounds which have not yet been separated (Lasantsch, *Deut. Chem. Ges. Ber.* iv. 404).

**Oxydiphenyl, Hydroxyldiphenyl, Diphenylic Phenol, or Diphenol**,  $C^{12}H^{10}O = C^{12}H^8OH = C^6H^5-C^6H^5OH$ . This compound is formed by heating potassium diphenylsulphonate,  $C^{12}H^8SO^2K$ , with potassium hydrate (Latschinoff, *Deut. Chem. Ges. Ber.* vi. 194), or by the action of potassium nitrite on monamidodiphenylsulphonate (Osten, *ibid.* vii. 170). It crystallises in colourless glistening plates, volatilises with vapour of water, sublimes easily, and gives a fine green colour with strong sulphuric acid (Osten). It dissolves readily in alcohol of 40 p.c., in ether, and in caustic potash; gives no coloration with ferric chloride; is not attacked by ammoniacal silver nitrate even at the boiling heat; gives with lead acetate a precipitate soluble in acetic acid (Latschinoff).

Nitric acid converts it mono- and dinitro-oxydiphenyl, the former of which melts at  $67^{\circ}$  and volatilises with vapour of water, while the latter melts at  $154^{\circ}$  and does not volatilise with vapour of water (Latschinoff).

With *benzoyl chloride* oxydiphenyl forms *benzoyl-oxydiphenyl*,  $C^{18}H^{14}O^2 = C^{12}H^8OC^6H^5O$ , which melts at  $132^{\circ}$  and dissolves with difficulty in alcohol and in ether (Latschinoff).

**Diphenylsulphonic Acids** (Engelhardt & Latschinoff, *Deut. Chem. Ges. Ber.* iv. 561; Latschinoff, *ibid.* vi. 193). *Diphenyl* heated with sulphuric acid yields two sulpho-acids which may be partially separated by their potassium salts, the monosulphonate being the less soluble in water of the two, but more completely by means of their copper salts, the disulphonate being but slightly soluble even in boiling water.

*Potassium diphenylmonosulphonate*,  $C^{12}H^8SO^2K + H^2O$ , prepared from the copper salt, crystallises from alcohol of 40 p.c. in flat needles or long plates moderately soluble in water, easily in dilute alcohol. The *copper salt*,  $(C^{12}H^8SO^2)_2Cu + 6H^2O$ , crystallises in rhombs or prisms sparingly soluble in water, more easily in alcohol of 40 p.c. In absolute alcohol all the diphenylmonosulphonates dissolve but sparingly. The *barium and calcium* salts obtained by precipitation from the potassium salt are anhydrous.

*Diphenyl-disulphonic acid*,  $C^{12}H^4(SO^2H)^2$ , is the chief product obtained when *diphenyl* is heated with excess of sulphuric acid, and its salts are produced together with a sublimate of *diphenyl*, by the action of heat on the diphenylmonosulphonates, e.g.—



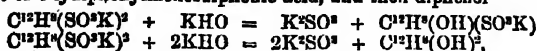
The *potassium salt* crystallises in thick laminae containing  $2\frac{1}{2}H^2O$ . Its solution is precipitated by barium chloride in the cold, by calcium chloride when heated.

By distilling the disulpho-acid with potassium cyanide, and boiling the residue with potash, a dicarbonic acid,  $C^{12}H^4(CO^2H)^2$ , is obtained.

*Diphenyl-disulphonic acid* or its potassium salt,\* fused with potash, yields first the

\* In the report of Latschinoff's paper (read before the Russian Chemical Society) in the *Berichte der Deutschen Chemischen Gesellschaft*, vi. 194, the salt concerned in this reaction is called "monodiphenylsulfonsäures Kalium," whereas it is clearly the disulphodiphenate; and on p. 195 of the same report the oxydiphenylmonosulphonate,  $C^{12}H^8(SO^2K)OH$ , is called "Mononitrodiphenylsulfonsäures Kalium."

potassium salt of oxydiphenylmonosulphonic acid, and then diphenol—



**Oxydiphenylsulphonic Acids.** Oxydiphenyl cautiously heated with sulphuric acid yields a mixture of mono- and disulphonic acid,  $\text{C}^{12}\text{H}_8(\text{SO}^3\text{H})(\text{OH})$ , and  $\text{C}^{12}\text{H}_8(\text{SO}^3\text{H})_2\text{OH}$ , which may be separated by means of their potassium salts, the mono-salts being less soluble than the corresponding di-salts. Ferric chloride gives no colour with the mono-salts, but a characteristic indigo colour with the di-salts. The mono-acid and its salts are converted by further heating with sulphuric acid into the di-salts.

**Potassium Oxydiphenylmonosulphonate.**  $\text{C}^{12}\text{H}_8(\text{SO}^3\text{K})(\text{OH}) + \text{H}^2\text{O}$  or  $\text{C}^{12}\text{H}_8\text{SO}^3\text{K} \cdot \text{C}^6\text{H}_5\text{OH} + \text{H}^2\text{O}$ , dissolves easily in weak potash-ley, not however forming a basic salt; also in boiling water, sparingly in cold water, most easily in boiling alcohol of 40 p.c. By distillation it yields oxydiphenyl and potassium oxydiphenyl-disulphonate—

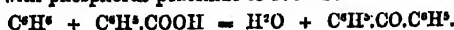


The barium, calcium, copper, and lead salts, are convertible into easily soluble basic salts; crystallise, some in laminæ, others in needles; dissolve sparingly in water and in alcohol; somewhat more readily in spirit of 40 p.c. The neutral barium salt contains  $1\text{H}^2\text{O}$ ; the neutral calcium salt,  $3\text{H}^2\text{O}$ . The potassio-cupric salt,  $[\text{C}^{12}\text{H}_8\text{SO}^3(\text{OH})]_2\text{K}^2\text{Cu} + 6\text{H}^2\text{O}$ , crystallises in green laminæ.

**Potassium Oxydiphenyl-disulphonate.**  $\text{C}^{12}\text{H}_8(\text{SO}^3\text{K})_2\text{OH} + 1\frac{1}{2}\text{H}^2\text{O}$  or  $\text{C}^{12}\text{H}_8(\text{SO}^3\text{K})_2 \cdot \text{C}^6\text{H}_5\text{OH} + 1\frac{1}{2}\text{H}^2\text{O}$ , obtained as above described, forms nodular groups of needles, easily soluble in water, precipitated from the solution by alcohol. Its solution forms no precipitate with barium, calcium, copper, or silver salts; with lead salts a scanty precipitate, probably of a basic salt, soluble in acetic acid. In presence of ammonia, basic salts are thrown down by solutions of barium, calcium, or lead salts.

**PHENYL ETHER.** See PHENYL OXIDE.

**PHENYL KETONES** (Kollarits a. Merz, *Deut. Chem. Ges. Ber.* v. 447; vi. 1035). *Diphenyl ketone* or *Benzophenone* (p. 176) is formed, together with a small quantity of a substance of high boiling point, by heating a mixture of benzene and benzoic acid with phosphorus pentoxide to  $180^\circ$ – $200^\circ$ :



The benzoic acid in this process may be replaced by benzoic anhydride, and the phosphoric anhydride by metaphosphoric, and even by pyrophosphoric acid, the yield in the latter case being, however, but small. Boron trioxide and dry hydrochloric acid do not act on benzene and benzoic acid, even at  $250^\circ$ .

*Chlorodiphenyl ketone*,  $\text{C}^{12}\text{H}_7\text{ClCO} \cdot \text{C}^6\text{H}_5$ , is obtained in like manner from chlorobenzene. It crystallises from a mixture of ether and alcohol in flat needles resembling benzoic acid, and from petroleum-naphtha in needles grouped in globular masses, melting at  $75.5^\circ$ – $76^\circ$  and boiling above  $300^\circ$ .

*Bromodiphenyl ketone*,  $\text{C}^{12}\text{H}_7\text{BrCO} \cdot \text{C}^6\text{H}_5$ , is obtained from bromobenzene, and has great resemblance to the preceding compound. It melts at  $81.5^\circ$ .

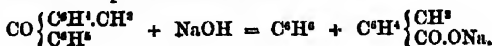
*Dinitro-diphenyl ketone*,  $\text{C}^{12}\text{H}_7\text{NO}_2\text{CO} \cdot \text{C}^6\text{H}_4\text{NO}_2$ , is formed by boiling dinitro-diphenylmethane with chromic acid solution; it is also obtained by the nitration of benzophenone, and is identical with that which Linnemann obtained by the action of nitric acid on benzhydrol. It crystallises from a mixture of alcohol and ether in small, shining needles, melting at  $129.5^\circ$  (W. H. Doer, *Deut. Chem. Ges. Ber.* v. 796).

*Isonitro-diphenyl ketone* is not produced in the nitration of benzophenone, but is formed by oxidising isodinitro-diphenylmethane. It is soluble in alcohol, ether, benzene, and acetic acid. From alcohol it crystallises in short straw-coloured needles or pale-yellow prisms; it melts at  $118^\circ$  (Doer).

*Diamido-diphenyl ketone*, identical with Laurent's and Chancel's *flavine* (ii. 656), forms long, pale-yellow needles, melting at  $165^\circ$ . The corresponding iso-compound could not be obtained in the pure state (Doer).

*Tolyl-phenyl Ketone*,  $\text{C}^{11}\text{H}_7\text{CO} \cdot \text{C}^6\text{H}_5$ , is obtained by heating toluene with benzoic acid and phosphorus pentoxide to  $180^\circ$ – $200^\circ$  for 8–10 hours. It is first obtained as an acid liquid, from which, after some time, long pointed plates separate out, which crystallise from a mixture of ether and petroleum-naphtha in large thick prisms resembling celestine, and melting at  $56.5^\circ$ – $57^\circ$ . It is readily soluble in ether and benzene, sparingly in petroleum-naphtha, and little more freely in alcohol. By oxidation with

chromic acid it yields benzoyl-benzoic acid, and therefore appears to be identical with Zincke's tolyl-phenyl ketone, although the latter compound is, according to this chemist, an oily liquid. When the solid ketone is heated with soda-lime to  $260^{\circ}$ – $270^{\circ}$ , it is resolved into benzene and paratoluic acid:



The portion of the ketone which remains liquid on standing yields also a large quantity of paratoluic acid; orthotoluic acid could not be detected.

*Cynyl-phenyl Ketone*,  $\text{C}^{10}\text{H}^{12}\cdot\text{CO}\cdot\text{C}^6\text{H}^5$ , is obtained in small quantity only, by heating camphor cymene with benzoic acid and phosphorus pentoxide. It is a pale yellow oil, having a very agreeable odour, and boiling at about  $340^{\circ}$ . It does not solidify in a freezing mixture, but becomes very viscid (Kollarits a. Merz).

*$\alpha$ - and  $\beta$ -Naphthyl-phenyl Ketone*,  $\text{C}^{10}\text{H}^7\cdot\text{CO}\cdot\text{C}^6\text{H}^5$ .—These two isomerides are formed together by heating naphthalene with benzoic acid and phosphorus pentoxide for 10–12 hours to  $200^{\circ}$ – $220^{\circ}$ . The  $\alpha$ -compound crystallises from a mixture of ether and alcohol in thick short prisms melting at  $77.5^{\circ}$ ; the  $\beta$ -compound forms needles melting at  $82^{\circ}$ . By separating the two kinds of crystals mechanically and recrystallising them, they may be obtained pure. When  $\alpha$ -naphthoic acid is heated with benzene and phosphorus pentoxide, only a small quantity of the  $\alpha$ -ketone is produced, besides carbon dioxide, naphthalene, and  *$\alpha$ -dinaphthyl ketone*. The latter compound is a glassy mass, which by recrystallisation, first from a mixture of ether and alcohol, and then from alcohol alone, yields colourless pointed needles melting at  $135^{\circ}$  and distilling without decomposition. It is also produced by heating naphthalene with  $\alpha$ -naphthoic acid and phosphorus pentoxide.  $\beta$ -naphthoic acid and benzene give a good yield of  $\beta$ -naphthyl-phenyl ketone.  *$\beta$ -dinaphthyl ketone* is formed by heating  $\beta$ -naphthoic acid with naphthalene and phosphorus pentoxide to  $200^{\circ}$ – $220^{\circ}$  for 20 hours. It crystallises from hot alcohol in plates, which soon separate into needles. It is less soluble in alcohol than the  $\alpha$ -compound, and melts at  $134.6^{\circ}$ – $135^{\circ}$ . According to theory, three dinaphthyl ketones may exist. The third modification appears to be formed by distilling a mixture of potassium  $\beta$ -naphthalene-sulphonate and oxalate; it melts at  $140^{\circ}$  (Kollarits a. Merz).

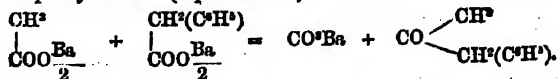
*Phenyl-methyl Ketone or Acetophenone*,  $\text{CH}^3\cdot\text{CO}\cdot\text{C}^6\text{H}^5$ , forms two nitro-derivatives, one solid and the other liquid, the latter of which, when heated with soda-lime and zinc-dust, yields a small quantity of indigo-blue (p. 606).

When boiling acetophenone is treated with dry ammonia and the product is distilled, a thick oil passes over first, and then a crystalline substance partially soluble in hydrochloric acid. Ammonia added to this solution throws down a base called acetophenonine,  $\text{C}^8\text{H}^{10}\text{N}$ , or  $\text{C}^8\text{H}^8\text{N}^2$ , which crystallises from hot alcohol in fine, interlaced needles melting at  $130^{\circ}$ . It is a very stable compound, not being decomposed by red-hot soda-lime or by a boiling solution of chromic acid. It is not produced by heating acetophenone with alcoholic ammonia.

*Acetophenonine hydrochloride* forms small, thin plates, and is decomposed by water. *Nitro-acetophenonine*,  $\text{C}^8\text{H}^{10}(\text{NO}^2)\text{N}$  [?], crystallises from hot ether in yellowish needles.

The portion of the product of the action of ammonia and phosphorus pentoxide on acetophenone, which is insoluble in acids, consists of triphenyl-benzene,  $\text{C}^6\text{H}^5(\text{C}^6\text{H}^5)^3$  (p. 945), (Engler a. Heine, *Deut. Chem. Ges. Ber.* vi. 638).

*Methyl-phenylmethyl Ketone, Benzyl-methyl Ketone, or Phenyl-acetone*,  $\text{CH}^3(\text{C}^6\text{H}^5)\cdot\text{CO}\cdot\text{CH}^3$ , is produced, together with acetone, diphenyl-acetone, toluene, and an empyreumatic oil, by the dry distillation of a mixture of equal parts of acetate and phenyl-acetate (alpha-toluete) of barium:



The ketone, purified by fractional distillation, boils at  $215^{\circ}$ , and has a specific gravity of 1.010 at  $3^{\circ}$ . It unites with sodium bisulphite, forming a compound which may be crystallised from dilute alcohol. When it is heated with phosphorus pentachloride, and afterwards with alcoholic potash, a hydrocarbon appears to be formed (R. Otto, *J. pr. Chem.* [2], i. 144).

*Diphenyl-methyl Ketone, Dibenzyl Ketone, or Diphenyl-acetone*,  $\text{CO} \begin{Bmatrix} \text{CH}^2(\text{C}^6\text{H}^5) \\ \text{CH}^2(\text{C}^6\text{H}^5) \end{Bmatrix}$ , is formed by the dry distillation of barium phenylacetate. The distillate, which solidifies at low temperatures, may be purified by pressure and crystal-

lisation from alcohol. It forms transparent flattened prisms an inch long, melts at 30° and boils at 320°. The fused mass solidifies in stellate groups of long needles (Engler & Heine).

**PHENYL OXIDE**,  $C^6H^5O = C^6H^5.O.C^6H^5$ . This body, isomeric with oxydiphenyl, was first obtained by List & Limpricht by the dry distillation of cupric benzoate (iv. 417), and has been more completely examined by Hofmeister (*Deut. Chem. Ges. Ber.* iii. 747), who obtains it also by the action of diazobenzene sulphate on phenol. Aniline sulphate is rubbed to a paste with water; a rapid stream of nitrous acid is passed through it; the solution is mixed with phenol; the mixture, after standing for some time, is carefully heated till all the nitrogen has escaped, then treated with caustic soda; the undissolved portion is distilled with vapour of water, as long as an oil passes over, and this oil is purified by rectification. The reaction is as follows:



In preparing phenyl oxide by the process of List & Limpricht, Hofmeister mixes the crude distillate with soda-ley, and distils it over an oil-bath with addition of water.

Phenyl oxide is a colourless solid mass having an odour of geraniums; melting at 28° and boiling at 246°; nearly insoluble in water, easily soluble in alcohol, benzene, and glacial acetic acid, miscible with ether.

Phenyl oxide is not decomposed by passing over red-hot zinc-dust, or by heating with hydriodic acid. Heated to 220° for 10 hours with pentachloride and oxychloride of phosphorus, it yields a chlorinated oil boiling at 260°–280°. On agitating it with strong sulphuric acid, the chief product obtained is a disulphonic acid (*infra*); if, however, the phenyl oxide is not quite pure, diphenyl is at the same time produced.

**Dibromophenyl oxide**,  $C^6H^4Br^2O$ , produced by the action of bromine on phenyl oxide dissolved in carbon sulphide, dissolves easily in alcohol, ether, benzene, and glacial acetic acid, and crystallises from alcohol in long, colourless, shining needles melting at 53°–55°.

**Dinitrophenyl oxide**,  $C^6H^4(NO^2)^2O$ , produced by the action of fuming nitric acid on phenyl oxide, forms long silky needles which melt at 135° and dissolve easily in alcohol, ether, benzene, and glacial acetic acid.

**Diamidophenyl oxide**,  $C^6H^4(NH^2)^2O$ , formed by the action of tin and hydrochloric acid on the dinitro-compound, crystallises in nearly colourless scales which become dark-coloured on exposure to moist air, and melt at about 185°. The sulphate crystallises in fine needles.

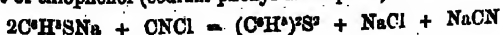
**Phenyl-oxide-disulphonic acid**,  $C^6H^5SO^2O = C^6H^5(SO^2H) - O - C^6H^5(SO^2H)$ .—This acid, isomeric with oxydiphenyl-disulphonic acid (p. 939), is obtained by heating phenyl oxide with sulphuric acid, as a colourless syrupy liquid, which evaporated in the exsiccator, deposits large hard crystals, deliquescent in the air, easily soluble in alcohol, insoluble in ether. The **barium salt**,  $\begin{matrix} C^6H^5SO^2 \\ C^6H^5SO^2 \end{matrix} BaO$  (dried at 120°) is a crystalline powder which dissolves slowly but abundantly in water; it contains water of crystallisation. The **sodium salt**,  $(C^6H^5SO^2Na)^2O$ , forms microscopic rhombic plates containing water of crystallisation. The **silver salt** crystallises in warty groups; the **lead salt** in slender needles (Hofmeister).

**Phenyl-allyl Oxide**,  $C^6H^5.CO.C^3H^5$ . See ALLYL ETHERS (p. 56).

**Phenyl-benzyl Oxide**,  $C^6H^5.CO.C^6H^5$ . See BENZYL ETHERS (p. 180).

**PHENYL SULPHIDES**. The **monosulphide**,  $(C^6H^5)^2S$ , passed several times through an iron tube filled with nails and heated to low redness, is converted, with separation of a large quantity of carbonaceous matter, into an isomeric compound, **paraphenyl sulphide**, which may be purified by distilling the crude product, cooling the distillate to a low temperature, and recrystallising the solid substance which separates out. It is insoluble in water, moderately soluble in carbon sulphide, ether, and benzene. By digestion with chromic acid mixture it is converted, analogously to phenyl sulphide, into **parasulphobenzide**,  $C^6H^5SO^2$ . This latter melts at 230°, and crystallises from hot alcohol in long, white, shining needles, soluble in benzene, ether, and carbon bisulphide. By hot concentrated sulphuric or nitric acid, it is not decomposed, but simply dissolved (Stenhouse, *Proc. Roy. Soc.* xviii. 542).

**Phenyl bisulphide**,  $(C^6H^5)^2S^2$ , is formed: a. By the action of cyanogen chloride on the sodium salt of thiophenol (sodium phenyl-mercaptide):



(Clamm, *J. pr. Chem.* [2], i. 147).

**β.** By subjecting the mercury-compound of thiophenol ( $C^6H^5$ ) $^2$ Hg to dry distillation or heating it with water to 180°, whereby it is resolved into mercury and phenyl bisulphide. This compound forms small white shining needles, which melt at 60°, and are converted by zinc and hydrochloric acid into thiophenol (Dreher & Otto, *Ann. Chem. Pharm.* cliv. 178).

**PHENYLAMINES. 1. Monophenylamine. Aniline,  $C^6H^5.NH^2$ .** *Solidifying point.* According to E. Lucius (*Deut. Chem. Ges. Ber.* v. 154), whose results are confirmed by Hofmann, aniline solidifies and remelts at -8°, not at -20° as commonly stated.

*Combinations.*—**α.** With Metallic Iodides.—On mixing alcoholic solutions of aniline and zinc iodide, the compound  $2C^6H^5.N.ZnI^2$  is formed, as a crystalline magma which dissolves at the boiling heat; and the solution on cooling deposits the compound in strongly lustrous, colourless prisms and needles, which dissolve readily in alcohol, but are partially decomposed by solution in water. It is decomposed by heat, giving off aniline and afterwards vapours of iodine. The cadmium-compound,  $2C^6H^5.N.CdI^2$ , prepared in like manner, forms long brilliant needles. The mercury-compound,  $2C^6H^5.N.HgI^2$ , is prepared by dissolving mercuric iodide in a boiling solution of aniline, and separates on cooling in sulphur-yellow plates and prisms. It cannot be purified by recrystallisation from alcohol, since it decomposes immediately on solution, with separation of a bright vermilion-coloured crystalline precipitate. The yellow salt is insoluble in water, easily soluble in aniline and in alcohol containing aniline. When exposed to the air it gives off aniline and acquires a vermilion colour. When carefully melted in a test-tube it solidifies on cooling to a crystalline mass, exhibiting on isolated spots beautiful vermilion-coloured crystalline vegetations (H. Vohl, *Arch. Pharm.* [2], cxlviii. 201).

**β.** With Organic Acids.—Aniline mucate,  $C^6H^5.O^2(C^6H^5.N)^2$ , is formed by boiling mucic acid with water and aniline: also together with phenyl-mucamide,  $C^6H^5.O^2(NHC^6H^5)^2$ , by heating mucic acid with excess of aniline (p. 948). It forms faintly yellow crystals, which dissolve in water and lose aniline on prolonged heating therewith, apparently without forming an acid salt. It is insoluble in boiling alcohol, but gives off the whole of its aniline on prolonged treatment with the boiling liquid. When heated with alkalis it yields alkaline mucates and free aniline. Heated in an air-bath it loses water, and is converted into phenylmucamide:



By dry distillation it is resolved into aniline, water, carbon dioxide, and phenylpyrrol (Kötnitz, *J. pr. Chem.* [2], vi. 136).

Aniline saccharate forms a syrupy mass yielding by dry distillation an oil which solidifies to a crystalline mass, and is obtained in white laminae by recrystallisation from alcohol (Kötnitz, *Chem. Centr.* 1870, 143).

*Reactions.*—1. Aniline vapour passed over heated lead oxide yields a small quantity of a base which crystallises in needles and melts at 70° (Behr & van Dorp, *Deut. Chem. Ges. Ber.* vi. 755).

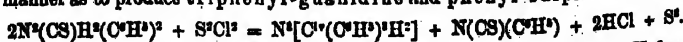
2. Commercial aniline heated with phosphorus and a little water, yields aniline-red, hydrogen phosphide being formed and the aniline being oxidised by the liberated oxygen (A. Stiasny, *Dingl. polyt. J.* xcix. 413).

3. When aniline in excess is boiled with sulphur as long as hydrogen sulphide continues to be evolved, thioaniline,  $C^6H^5.N^2S = S(C^6H^5.NH^2)^2$ , is formed, together with a large quantity of resinous matter, probably containing more highly sulphuretted anilines (Morz & a. Weith, *Deut. Chem. Ges. Ber.* iii. 978).

4. When aniline is treated with pure sulphur chloride,  $S^2Cl^2$ , diluted with carbon bisulphide, a reaction takes place in two stages, in the first of which, phenylsulphocarbamide (sulphocarbaniide), aniline hydrochloride, and free sulphur are formed, according to the equation:



and in the second, the excess of sulphur chloride acts on the sulphocarbaniide in such a manner as to produce triphenyl-guanidine and phenyl-sulphocarbimide:

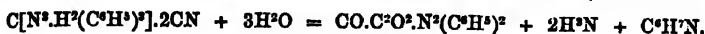


This last reaction is exactly similar to that which was observed by Hofmann (1st Suppl. 686) to take place between sulphocarbaniide and iodine (Claus & Krall, *Deut. Chem. Ges. Ber.* iv. 147).

5. Aniline acetate, dissolved in acetic acid, is violently attacked by chromic oxychloride, and the product, diluted with water, yields on distillation a very turbid yellow distillate, from which needle-shaped crystals separate; these, however, disappear

after a while, and the solution then no longer contains any crystallisable compound (Carstanjen, *J. pr. Chem.* [2], ii. 82).

6. With *cyanogen*, aniline forms, together with aniline cyanide, a red crystalline mass which, when purified, yields fine red crystals of a mono-acid base, having the formula  $C^6H^5N^+$ , and forming with hydrochloric acid the crystalline salt  $C^6H^5N^+HCl$ . This body may be regarded as triphenyl-guanidine cyanide, and represented by the formula  $N^+[C^6H^4(C^6H^5)^3].2CN$ . When heated with weak spirit (bost under pressure) this base is resolved into diphenylparabanic acid, ammonia, and aniline:



On boiling the alcoholic solution of the base with concentrated hydrochloric acid for some time, the diphenylparabanic is also decomposed, and ultimately ammonia, aniline, carbon dioxide, and oxalic acid are produced (Hofmann, *Deut. Chem. Ges. Ber.* iii. 763).

7. With *carbon tetrabromide*, aniline forms hydrobromide of triphenyl-guanidine (Bolas a. Groves, p. 257):

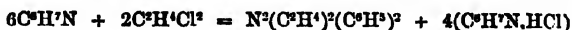


8. Aniline, added by small quantities to *chloracetyl chloride*, which must be kept cool, forms phenyl-chloracetamide, which crystallises from aqueous solution in slender needles and from alcohol in plates:



(Tommasi, *Compt. rend.* lxvi. 885).

9. Aniline, heated to  $150^{\circ}$ – $170^{\circ}$  with *ethylidene-chloride*, forms diethylidene-diphenyl-diamine (also produced by the action of aldehyde on aniline, iv. 456):



(H. Schiff, *Deut. Chem. Ges. Ber.* iii. 412).

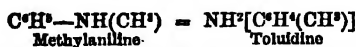
10. With *chloral*, aniline appears to form basic compounds (Wallach, *ibid.* iv. 668); see also Maumené (*Bull. Soc. Chim.* [2], xiii. 409).

11. Aniline containing potassium in solution forms, with *bromobenzene*, a comparatively small quantity of diphenylamine, and a larger quantity of triphenylamine (Merz a. Weith, *Deut. Chem. Ges. Ber.* v. 646).

12. When aniline hydrochloride is heated to  $230^{\circ}$ – $250^{\circ}$  for several hours with *methyl alcohol*, a yellow transparent honey-like mass is formed, consisting chiefly of methylaniline hydrochloride:

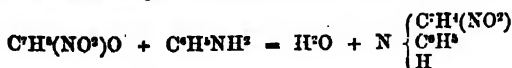


and on heating the contents of the tube for a day, this mass is converted by intramolecular transposition into the crystalline hydrochloride of toluidine (Hofmann, *ibid.* v. 720):

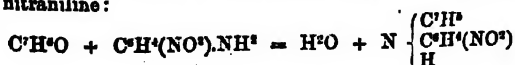


13. A mixture of aniline, aniline hydrochloride, and *furfural*, all in alcoholic solution, solidifies to crystals of the hydrochloride of furfuraniline,  $C^6H^5O.N^+HCl$ . Other salts of this base are obtained in like manner. The base itself, separated by triturating its salts with ammonia and kneading with water, forms a brown mass. Its alcoholic solution decomposes in contact with the air, and then no longer forms crystallisable salts with acids (Stenhouse, *Proc. Roy. Soc.* xviii. 537).

14. With *nitrobenzoic aldehyde*, aniline forms nitrobenzenylanilide,\*  $C^6H^5N^+O^2$ :

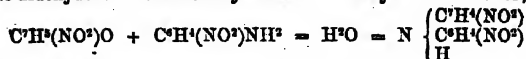


An isomeric compound, benzenyl-nitranilide, is formed by the action of benzoic aldehyde on nitraniline:



\* Called, in the original paper, *nitrobenzenylanilide*

Nitrobenzoic aldehyde and nitraniline yield nitrobenzyl-nitranilide,  $C^6H^4N^2O^4$ :



Lazorenco (*N. Petersb. Acad. Bull.* xv. 372).

**Bromaniline**,  $NH^2(C^6H^4Br)$ , (Fittig & Mager, *Deut. Chem. Ges. Ber.* vii. 1175). *Parabromaniline* was prepared from the nitrobromobenzene obtained by nitration of metabromobenzene, by reduction with tin and hydrochloric acid, and distillation of the solution mixed with caustic soda. When purified by crystallisation from aqueous alcohol, it forms large colourless regular octohedrons, melting at  $63^\circ$ , decomposed by distillation. The monobromophenol obtained from this bromaniline by the diazo-reaction melts at  $63^\circ$ – $64^\circ$ , boils at  $238^\circ$ , and is converted by fusion with potash into resorcin.

*Orthobromaniline*, obtained in like manner by nitration of orthobromobenzene, &c., melts at  $31^\circ$ – $31.5^\circ$ , boils at  $229^\circ$ , and distils without decomposition.

**Chloraniline**,  $NH^2(C^6H^4Cl)$ . An alcoholic solution of this base, heated with carbon sulphide, yields a sulphurea,  $CS(NH.C^6H^4Cl)^2$ , which crystallises from alcohol in long white needles, melting at  $166^\circ$  (Losanitsch, *ibid.* v. 156).

**Nitraniline**,  $NH^2(C^6H^4NO^2)$ . Of the three possible modifications of this base, two have long been known, viz.: orthonitraniline (1 : 2) from acetanilide, and metanitraniline (1 : 3) from dinitrobenzene (p. 925).<sup>\*</sup> The third, or paranitraniline (1 : 4), has lately been obtained by Walker & Zincke (*ibid.* v. 114), by heating paranitrobenzene (p. 142) to  $180^\circ$ – $190^\circ$  with concentrated alcoholic ammonia, then evaporating to dryness, and recrystallising from water.

Paranitraniline is distinguished from the other two modifications by its melting point, solubility, and the colour of its salts. It is much more soluble than the ortho- and meta-modifications in water and in alcohol; its solutions are intensely yellow, and communicate this colour to the skin. It volatilises more easily with vapour of water, and the watery distillate has a strong yellow colour. The melting points of the three nitranilines are as follows:

	Ortho- 146°	Meta- 108°	Para- 66°
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Paranitraniline, heated between two watch-glasses, yields a sublimate of oily drops which become crystalline. Like the other two nitranilines, it forms unstable salts which, however, are not colourless, but distinctly yellow.

**Diphenylamine**,  $C^6H^5N = NH(C^6H^5)^2$ . According to Dusart & Bury (*Compt. rend.* lxxiii. 1276), this base is produced by the action of various phenol-compounds on aniline, the reaction consisting in the substitution of phenyl derived from the phenolic ether for an atom of hydrogen in the aniline molecule; thus—*a.* By heating aniline to  $225^\circ$  with dry sodium phenylsulphonate. *B.* By heating a mixture of 1 pt. aniline hydrochloride, 2 pts. phenol, and 1 pt. fuming hydrochloric acid to  $250^\circ$ ; in the absence of the acid the reaction takes place only at  $300^\circ$ , showing that the acid acts as an etherifying agent. *γ.* By passing aniline and phenyl bromide (bromobenzene) through a tube heated to low redness, or by the action of sodium on the same mixture at ordinary temperatures; also by heating aniline to  $180^\circ$  with phenyl iodide. Girard & De Laira on the other hand (*Compt. rend.* lxxiv. 811, 1264), find that diphenylamine is not produced by heating dry sodium phenylsulphonate with aniline, unless a small quantity of an aniline salt is also present, in which case its formation is due to the action of the aniline salt on the aniline itself. Similarly the formation of diphenylamine on phenyl bromide or iodide occurs only when this iodide or bromide contains free acid, or when the aniline contains an aniline salt. Lastly Girard & De Laira were unable to obtain diphenylamine by heating aniline with phenyl chloride. They therefore conclude that diphenylamine is not produced by the substitution of a phenolic residue for an atom of hydrogen in aniline. See, on the contrary, Merz & Weith, *infra*.

According to Merz & Weith (*Deut. Chem. Ges. Ber.* v. 288) commercial diphenylamine is pure, with the exception of traces of aniline; it crystallises from ligroin in large plates, like naphthalene, and melts at  $54^\circ$ .

It is slowly acted upon by concentrated sulphuric acid at  $150^\circ$ – $160^\circ$ , and converted into a mixture of *diphenylamine-monosulphonic* and *-disulphonic acids*, which may be separated by fractional crystallisation of the barium salts, since the salt of the monosulpho-acid is difficultly soluble, while that of the disulpho-acid is easily soluble in water. The action of oxidising agents on the solution of these sulpho-acids, or their salts, gives rise to a variety of characteristic colorations.

<sup>\*</sup> Hitherto regarded as paranitraniline (p. 145), (inasmuch as the dinitrobenzene, lately shown to have its two nitro-groups in the relative positions (1 : 3), was formerly regarded as a *para*-compound (see p. 928).



*Acetyldiphenylamine*,  $N(C^6H^5)_2C^2H^3O$ , is obtained by the action of acetyl chloride on diphenylamine.

Carbon disulphide has no action on diphenylamine.

Chlorocarbonic ether and diphenylamine give the compound,  $N(C^6H^5)_2.COOCCl^2H^3$ .

*Diphenylamine as a test for Nitrous and Nitric acids.*—The reagent is prepared by pouring pure sulphuric acid over a few crystals of diphenylamine, and adding a little water, whereby the temperature is somewhat raised and the crystals are dissolved; the solution is then mixed with a larger quantity of pure acid. This clear colourless liquid at once produces a beautiful and very permanent blue coloration in ordinary sulphuric acid of  $60^\circ$  or  $66^\circ$  B., or in chamber acid ( $52^\circ$  B.), containing even traces of nitrous acid. The reaction is at least as delicate as that with ferrous sulphate.

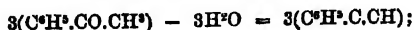
The test may be rendered quantitative by comparing the coloration produced respectively by 1 c.c. of the acid to be tested, and 1 c.c. of acid containing a known amount of nitrous acid with an excess of the reagent (a solution of 1 gram diphenylamine in 1 litre of pure sulphuric acid), and adding pure sulphuric acid to one or other of the solutions until the intensity of colour is alike in both cases. Although not absolutely accurate, the method is sufficiently so for most technical purposes, and is far simpler than many of the methods ordinarily employed (E. Kopp, *Deut. Chem. Ges. Ber.* v. 284).

**Triphenylamine**,  $C^{18}H^{15}N = N(C^6H^5)_3$ , is produced, together with a comparatively small quantity of diphenylamine, by the action of bromobenzene on aniline. It is sparingly soluble in alcohol, more readily in petroleum-naphtha, and crystallises in large thick plates, melting at  $126^\circ$ – $127^\circ$ , and boiling at a high temperature. With different reagents it gives blue or green colours. Triphenylamine may also be obtained by the same reaction from diphenylamine (Merz a. Weith, *ibid.* v. 646).

**PHENYL-BENZENES.** *Diphenyl-benzene*,  $C^{18}H^{14} = C^6H_4(C^6H^5)_2$ , is formed, together with diphenyl and large quantities of yellow brominated products, by the action of sodium on an ethereal solution of solid dibromobenzene, or better of a mixture of this compound with monobromobenzene. To obtain it pure, the ethereal solution is mixed with water; the diphenyl distilled off; and the crystalline residue dried, distilled in a stream of carbonic anhydride, pressed between paper, and recrystallised from ligroin and benzene.

Diphenyl-benzene melts at  $201^\circ$  (corr.  $205^\circ$ ), sublimes readily, and boils in the vapour of boiling sulphur ( $440^\circ$ ). It is insoluble in boiling alcohol, nearly insoluble in ether, somewhat more soluble in ligroin, and still more in benzene. From the latter solvent it crystallises in tufts of flat needles. It does not combine with picric acid (F. Riese, *Zeitschrift f. Chem.* [2], vi. 102, 735).

*Triphenyl-benzene*,  $C^{24}H^{18} = C^6H_2(C^6H^5)_3$ , is formed by the action of phosphorus pentoxide on acetophenone, in the same manner as mesitylene (trimethyl-benzene) from acetone:



also, together with acetophenone, by the action of dry ammonia and phosphorus pentoxide on boiling acetophenone; in this case it constitutes the portion of the product which is insoluble in acids (p. 940).

Triphenyl-benzene crystallises from ether in short, well-defined prisms melting at  $167^\circ$ – $168^\circ$ . It is but slowly attacked by oxidising agents. With bromine and nitric acid it forms substitution-products (Engler a. Heine, *Deut. Chem. Ges. Ber.* vi. 838).

**PHENYL-BIURETS.** See BIURET (p. 193).

**PHENYL-BROWN.** This colouring matter, which possesses explosive properties, is formed by the action of strong nitric and sulphuric acid on phenol. From the experiments of Bolley a. Hammett (*Dingl. pol. J.* cxv. 150), it appears to be a mixture of dinitrophenol with a brown amorphous substance, which may be dissolved out by alkalis and precipitated by alcohol, and is not at all explosive. The explosive character of the phenyl-brown is therefore due to the dinitrophenol.

**PHENYL-BUTYLENE**,  $C^{14}H^{12} = C^6H_5(C^4H^7)$  (Aronheim, *Deut. Chem. Ges. Ber.* v. 1068). This hydrocarbon is formed by mixing benzyl chloride with allyl iodide in ethereal solution, the action commencing at ordinary temperatures, but requiring the heat of the water-bath for its completion. The liquid portion of the product, fractionated in Linnemann's apparatus (p. 436), yields, first diallyl, and then phenyl-butylene passing over between  $176^\circ$  and  $178^\circ$ , the residue in the retort consisting chiefly of dibenzyl.

Phenyl-butylene is a colourless aromatic oil having an odour like that of unsaturated hydrocarbons, and a specific gravity of 0.915 at  $15.5^\circ$ . The direct action of bromine on it gives rise to the separation of hydrobromic acid, but on adding bromine to its

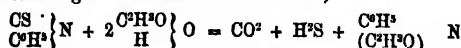
## 946 PHENYL-URETHANES—PHENYLENE-DIAMINE.

solution in chloroform, combination takes place, producing the bromide  $C^6H^4Br^2$ , in the form of an oil which distills without change. On treating this bromide with potash, hydrogen bromide is separated; but the formation of the hydrocarbon,  $C^6H^4$ , has not been definitely established. By oxidation with dilute nitric acid phenyl-butylene yields an oil which smells like bitter almond oil, and a sublimate apparently consisting of benzoic and cinnamic acids.

**PHENYL-CARBAMIC ETHERS, or PHENYL-URETHANES.** On *Ethyl Phenylcarbamate* or *Carbanilate*,  $CO \begin{Bmatrix} NH.C^6H^5 \\ OC^2H^5 \end{Bmatrix}$ , see **CARBAMATES** (p. 252).

*Isobutyl Phenylcarbamate*,  $CO \begin{Bmatrix} NH.C^6H^5 \\ OC^4H^9 \end{Bmatrix}$ , is produced by mixing ethereal solutions of isobutyl chlorocarbamate and anilino. It crystallises in soft white needles, melting at  $80^\circ$  and boiling at  $216^\circ$ , a small portion being thereby resolved into isobutyl alcohol and phenyl-cyanate. It dissolves easily in alcohol and ether, sparingly in water (*E. Mylius, Deut. Chem. Ges. Ber. v. 972*).

**PHENYL-DIACETAMIDE**,  $N(C^6H^5)(C^2H^3O)^2$ , is formed by heating phenyl-sulphocarbimide with glacial acetic acid to  $130^\circ$ – $140^\circ$ ;



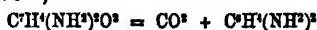
It resembles acetamide, melts at  $111^\circ$ , and is resolved by alkalis into anilino and acetic acid (*Hofmann, Deut. Chem. Ges. Ber. iii. 770*).

**DI-PHENYLENE KETONE**,  $CO \begin{Bmatrix} C^6H^5 \\ C^6H^5 \end{Bmatrix}$ . On the formation and constitution of this hydrocarbon, and its conversion into phenylbenzoic acid, see pp. 94, 95, 435.

By distillation over  *zinc-dust* , it is easily and completely reduced, forming a colourless hydrocarbon—doubtless diphenylene-methane,  $CH^2 \begin{Bmatrix} C^6H^5 \\ C^6H^5 \end{Bmatrix}$ —which dissolves easily in alcohol, and crystallises in shining scales or warty concretions melting at  $113^\circ$  (*Fittig, ibid. vi. 287*).

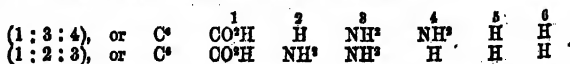
**DI-PHENYLENE OXIDE**,  $\begin{Bmatrix} C^6H^5 \\ C^6H^5 \end{Bmatrix} O$  (see p. 435).

**PHENYLENE-DIAMINE.** *Diamidobenzene*,  $C^6H^4N^2 = C^6H^4(NH^2)^2 = N^2 \begin{Bmatrix} H^1 \\ (C^6H^4) \end{Bmatrix}$ .—Two modifications ( $\alpha$  and  $\beta$ ) of this base were obtained by Hofmann, by the action of reducing agents on the corresponding nitramidobenzenes (nitranilines),  $C^6H^4(NO^2)(NH^2)$  (see iv. 980; *1st. Suppl. 923*). A third modification ( $\gamma$ ) is obtained by the following processes:—  
1. By distillation of either of the two diamidobenzoic acids produced from uramidobenzoic acid (*1st Suppl. 923*):



(*Griess, J. pr. Chem. [2], iii. 143*).

Now these two diamidobenzoic acids are derived from the same amidobenzoic acid (1 : 2), and their isomerism is explained by the following formula:

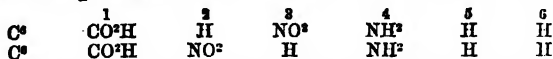


Consequently the phenylene-diamine formed from either of them will have the two groups  $NH^2$  in contiguous places; that is to say, it will be an *ortho*-compound (1 : 2). Now  $\beta$ -phenylene-diamine (from dinitrobenzene) is known to be the *meta*-compound, and therefore  $\alpha$ -phenylene-diamine must be the *para*-compound (1 : 4).

2. By boiling paradibromobenzene,  $C^6Br^2HHBr^2HH$ , with fuming nitric acid, treating the resulting nitrodibromobenzene (1 : 2 : 4) or  $C^6Br(NO^2)HHBr^2HH$ , with alcoholic ammonia, whereby it is converted into nitramidobromobenzene (1 : 2 : 4), that is either  $C^6(NH^2)(NO^2)HHBr^2HH$ , or  $C^6Br(NO^2)H(NH^2)HH$ , and reducing this last compound with tin and hydrochloric acid. The phenylene-diamine thus formed will have its two  $NH^2$  groups in the position 1 : 2 or 1 : 3; but the identity of its properties

with those of Griess's base shows that it is the ortho-compound (Meyer a. Wurster, *Deut. Chem. Ges. Ber.* v. 362); compare p. 144.

3. By heating nitranilic acid with ammonia to 160°, whereby the group  $\text{OCH}^3$  is replaced by  $\text{NH}^2$ ; reducing the resulting nitroparamidobenzoic acid with tin and hydrochloric acid, and subjecting the diamidobenzoic acid thereby produced to dry distillation. Now since anilic acid is methyl-paraoxybenzoic acid,  $\text{C}^6(\text{CO}^2\text{H})\text{HI}(\text{OCH}^3)\text{H}$ , the nitroparamidobenzoic acid formed from it must have the constitution represented by one of the following formulæ:



Consequently the diamidobenzoic acid and the phenylene-diamine derived from it will have the two  $\text{NH}^2$ -groups either contiguous (3 : 4 or 1 : 2) or separated by one interval (2 : 4 or 1 : 3). But this phenylene-diamine likewise agrees in properties with Griess's compound, and must therefore be regarded as the ortho-modification.

This conclusion is strengthened by the fact that when the nitroparamidobenzoic acid is treated with nitrous acid in alcoholic solution, it is converted, by substitution of H for  $\text{NH}^2$ , into ordinary nitrobenzoic acid,  $\text{C}^6\text{H}^4(\text{NO}^2)\text{CO}^2\text{H}$  (crystallising in needles which melt at 140°–141°, soluble in 400 pts. of water at 22.5°, yielding an ethylic ether which crystallises in plates melting at 40°–41°, and reduced by tin and hydrochloric acid to an amidobenzoic acid melting at 172°). Now since, in the formation of this acid from nitroparamidobenzoic acid, the  $\text{NH}^2$ -group is replaced by H, whereas, in the conversion of the same acid into phenylene-diamine, it is the  $\text{CO}^2\text{H}$ -group that is thus replaced, it is clear that whether the nitroparamidobenzoic acid be represented by the first or the second of the above formulæ, 1 : 3 : 4 or 1 : 2 : 4, the phenylene-diamine and nitrobenzoic acid derived from it cannot have their side-chains in the same relative position. If the first be a 1 : 2 compound, the second must be 1 : 3, and vice versa. Now, according to recent investigations (p. 133), ordinary nitrobenzoic acid (like its congeners amidobenzoic, oxybenzoic acid, &c.) is a meta-compound, 1 : 3, and therefore the phenylene-diamine in question must be an ortho-compound, 1 : 2 (H. Salkowski, *Deut. Chem. Ges. Ber.* v. 722).

4. Orthophenylene-diamine is also produced by the action of tin and hydrochloric acid on the nitraniline obtained from the bromonitrobenzene which melts at 38°, which must therefore be likewise an ortho-compound (Zincke a. Sintenis, *ibid.* vi. 123).

**Properties and Reactions.**—Orthophenylene-diamine dissolves readily in hot water and crystallises therefrom in white, or often reddish, quadratic plates; it is also very soluble in alcohol and in ether.

The melting and boiling points of the three phenylene-diamines are shown in the following table:

	Melting point	Boiling point
Orthophenylene-diamine . . .	99°	252° (Griess)
Meta- or $\beta$ -phenylene-diamine . . .	140	267 (Hofmann)
Para- or $\alpha$ -phenylene-diamine . . .	63	287 (Hofmann)

*Orthophenylene-diamine sulphate*,  $\text{C}^6\text{H}^4(\text{NH}^2)^2\text{SO}^4\text{H}^2 + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallises in shining scales easily soluble in hot, sparingly in cold water, and giving off their water of crystallisation at a few degrees above 100°. The *platinochloride* is a brown-red precipitate.

On adding a concentrated solution of ferric chloride to a solution of this diamine in hydrochloric acid, ruby-red needles separate, consisting of the hydrochloride of a base,  $\text{C}^6\text{H}^4\text{N}^4$ , which may be obtained by adding ammonia to the solution of the hydrochloride, in deep yellow microscopic needles, almost insoluble in all neutral solvents. The formation of this base is perhaps represented by the equation  $2\text{C}^6\text{H}^4\text{N}^2 + \text{O}^2 = 3\text{H}_2\text{O} + \text{C}^6\text{H}^4\text{N}^4$  (Griess).

According to Salkowski, orthophenylene-diamine, when oxidised by chromic acid mixture, gives off a strong odour of quinone; Meyer a. Wurster, on the other hand, did not observe this odour. Metaphenylene-diamine is known to yield quinone by oxidation; paraphenylene-diamine does not (iv. 481).

**PHENYL-GUANIDINES.** See GUANIDINE (p. 582).

**PHENYL-METHANES.** Diphenyl-methane or Benzyl-benzene,  $\text{C}^6\text{H}^5(\text{CH}^2\text{C}^6\text{H}^5)$ , is formed, together with other products, by heating benzyl chloride with benzene and zinc-dust (Zincke, *Deut. Chem. Ges. Ber.* iv. 298), also by sulphuric acid diluted with glacial acetic acid, on a mixture of benzyl alcohol and benzene (Meyer a. Wurster, *ibid.* vi. 963). Respecting its properties, see BENZYL-BENZENE (p. 183). On its reaction with formaldehyde, see p. 535.

**Substitution-derivatives of Diphenyl-methane** (W. H. Doer, *Deut. Chem. Ges. Ber.* v. 795). **Dinitro-diphenylmethane**,  $C^{12}H^{10}(NO^2)^2$ , is produced by dissolving the hydrocarbon in cold fuming nitric acid of sp. gr. 1.5. It is insoluble in water and alcohol, sparingly soluble in ether, and crystallises from hot benzene in long, brittle, ridgescent needles, melting at  $183^\circ$ . By oxidation with chromic acid mixture, it is converted into dinitro-diphenyl ketone or dinitrobenzophenone (p. 939).

**Isonitro-diphenylmethane**,  $C^{12}H^{10}(NO^2)^2$ , is formed when diphenylmethane is heated in a water-bath with nitric acid of sp. gr. 1.4. It is insoluble in water, but soluble in alcohol, ether, benzene, and acetic acid, and crystallises in small straw-coloured needles, showing a blue lustre and melting at  $172^\circ$ . By oxidation it is converted into isodinitrobenzophenone.

**Tetranitro-diphenylmethane**,  $C^{12}H^8(NO^2)^4$ , is the chief product formed by the action of a well-cooled mixture of concentrated nitric and sulphuric acid on diphenylmethane. It is insoluble in water, alcohol, and ether, sparingly soluble in benzene, a little more in glacial acetic acid, from which it crystallises in brilliant, pale-yellow, hard prisms, melting at  $172^\circ$ .

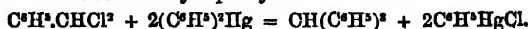
**Diamido-diphenylmethane**,  $C^{12}H^{10}(NH^2)^2$ , crystallises from alcohol in small pearly scales, melting at  $85^\circ$  and having the greatest resemblance to benzidine. The hydrochloride is very soluble in water and alcohol, and crystallises from dilute hydrochloric acid in small white plates. The sulphate is sparingly soluble in alcohol, and crystallises from water in small brilliant plates.

Isonitro-diphenylmethane and its salts are very unstable compounds which could not be obtained in the pure state.

**Diphenylmethane-disulphonic acid** is formed by dissolving the hydrocarbon in an excess of fuming sulphuric acid on a water-bath. The potassium salt,  $C^{12}H^{10}(SO^2K)^2 + H^2O$ , crystallises from dilute alcohol in small shining prisms. The barium salt is anhydrous, and crystallises from an aqueous solution in very small scales. The copper salt,  $C^{12}H^{10}(SO^2)^2Cu$ , is soluble in water and crystallises from dilute alcohol in small, green shining plates. The free acid,  $C^{12}H^{10}(SO^2H)^2$ , separates from an aqueous solution in small deliquescent plates, and from alcohol in arborescent needles melting at  $59^\circ$ .

Bromine acts violently on diphenyl-methane, forming a viscid substance, which, after standing for months, yields crystalline crusts forming large tables when recrystallised from ether. This body contains 4 atoms of bromine, but the quantity obtained was not sufficient to decide whether it is an addition- or a substitution-product.

**Triphenyl-methane**,  $CH(C^6H^5)^3$ , is obtained by heating 1 mol. of benzylene dichloride with 2 mols. of mercury-diphenyl:



It is a solid, melting at  $92.5^\circ$ , and boiling at about  $335^\circ$ . From an alcoholic solution it separates in brilliant, well-formed crystals; it is also readily soluble in ether and benzene, forming with the latter hydrocarbon the compound  $CH(C^6H^5)^3.C^6H^6$ . This compound forms large transparent crystals, which melt at  $76^\circ$ , and at this temperature, or when exposed to the air, give off the benzene and become white and opaque. Triphenyl-methane is also soluble in toluene, but does not combine with it. On dissolving it in warm fuming sulphuric acid, it is converted into the sulphonic acid,  $CH(C^6H^5)_3.SO^2H^2$ , the barium salt of which is precipitated by alcohol from an aqueous solution in fine white needles. No other salt could be obtained crystallised, but a concentrated solution of the free acid solidifies on standing to a crystalline mass (Kekulé a. Franchimont, *Deut. Chem. Ges. Ber.* vi. 186).

**PHENYL-MUCAMIDE**,  $C^6H^5O^2(NHC^6H^5)^2$  (Köttitz, *J. pr. Chem.* [2] vi. 136). This compound is formed, together with aniline mucate, by heating mucic acid with excess of aniline:



also by heating aniline mucate in an air-bath:



It is best prepared, however, by the action of aniline on an ether of mucic acid; ethyl mucate, for example.

Phenyl-mucamide forms small, very thin, white laminae, which are quite insoluble in water, alcohol, ether, benzene, carbon sulphide, glycerin, and dilute mineral acids. It is decomposed by boiling with strong potash, phenylamine being separated. Concentrated sulphuric acid converts it into a black mass. Fuming nitric acid dissolves it, forming a yellow solution, from which water throws down a yellow body, probably

a nitro-derivative. By dry distillation it yields phenyl-pyrrol,  $N(C^6H^5)(C^6H^5)$ . See PYRROL.

**PHENYL-NAPHTHYLAMINE.** See NAPHTHYLAMINE (p. 846).

**PHENYL PURPURIC ACID.** See PURPURIC ACID.

**PHENYL-TRIESTEIDE, STANNIC,**  $Sn(C^6H^5)(C^6H^5)^3$ . See STANNIC ETHIDES.

**PHENYL-UREAS.** See UREAS.

**PHENYL-URETHANE,**  $CO \begin{cases} NH.C^6H^5 \\ OC^6H^5 \end{cases}$ . See CARBAMATES (p. 252).

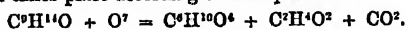
**PHENYL-XYLIDINE,**  $NH(C^6H^5)(C^6H^5)$ . See XYLIDINES.

**PHLOROGLUCIN,**  $C^6H^5O^3$ . This substance, treated with chlorine and water at ordinary temperatures, yields dichloroacetic acid (Hlasiwetz a. Habermann, *Ann. Ch. Pharm.* clv. 120).

**PHOLERITE.** A mineral from India named *Meerschaumite*, by Ross, has been recognised by Maskelyne a. Flight (*Chem. News*, xxii. 260) as pholerite, and found to consist of 43.144 p.c.  $SiO^2$ , 41.073  $Al^2O^3$  and 17.783 water.

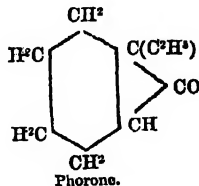
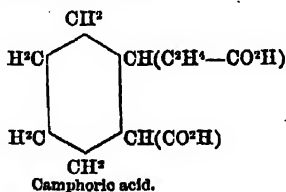
**PHORONE,**  $C^6H^{10}O$  (Kachler, *Ann. Ch. Pharm.* clxiv. 76). This body, the ketone of camphoric acid, obtained by distilling the calcium salt of that acid, is likewise produced from acetone by the action of quicklime or of sodium, and by heating cane-sugar or grape-sugar with lime (i. 733). Schwanert's *camphrene*, obtained by the action of sulphuric acid on camphor, and supposed by him to be identical with phorone, appears to have been a mixture (p. 238).

Phorone from camphoric acid (b. p.  $206^\circ$ – $215^\circ$ ), oxidised with chromic acid mixture, yields acetic acid, and an acid isomeric with adipic acid,  $C^6H^{10}O^4$ , which, after the acetic acid has been distilled off, may be dissolved out of the residue by agitation with ether. The reaction takes place according to the equation:



Phorone prepared from cane-sugar yields the same products by oxidation with chromic acid. The acid,  $C^6H^{10}O^4$ , is likewise formed, together with oxalic acid, by oxidising phorone with nitric acid.

The relation of phorone to camphoric acid may be represented by the following formulæ (compare p. 234):



**PHOSGENE.** See CARBON OXYCHLORIDE (p. 261).

**PHOSPHAMMITE.** This name is given by C. U. Shepard to ammonium phosphate found in the guano of the Guanape islands, Peru (p. 584).

**PHOSPHETHYL CYANIDE.** See PHOSPHINES.

**PHOSPHIDES, METALLIC.** These compounds are formed in the decomposition by heat of certain hypophosphites (p. 966); also in some cases by the action of phosphorus on metallic solutions (p. 959).

*Iron Phosphides.*—*Triferrous phosphide*,  $Fe^3P^2$ , is formed by pouring a solution of ferrous sulphate into a flask in which phosphoretted hydrogen is generated by heating phosphorus with potash-ley. The precipitate of ferrous hydrate produced in the first instance gradually turns grey, and finally black, by conversion into phosphide. The excess of phosphorus is removed by prolonged boiling with potash; the precipitate is boiled with strong hydrochloric acid to remove oxides and salts of iron; and the residual black powder is washed and dried in a stream of carbonic anhydride. As thus prepared it contains 71.74 to 72.17 p.c. iron and 28.48 to 27 phosphorus, agreeing approximately with the formula above given.

Triferrous phosphide dissolves very slowly in boiling hydrochloric acid alone; quickly, however, on addition of nitric acid. It is magnetic, and when recently prepared, takes fire in the air, even below  $100^\circ$  (Schenk, *Chem. Soc. J.* [2], xi. 826).

An octoferrous phosphide,  $Fe^8P^2$ , is formed according to Sidot (*Compt. rend.* lxxiv.

1425), by heating iron-wire in vapour of phosphorus, and repeatedly igniting the product in a crucible. It forms a metallic mass having the appearance of pig-iron, and on breaking it, the interior is often found to be studded with beautiful crystals about half an inch long and having the form of square prisms. It has a steel-gray colour, and is iridescent on the surface; is nearly as hard as steel, and strongly magnetic.

Daubrée (*ibid.* 1427) observes that Boblique, some years ago, prepared a phosphide of iron on the large scale from the nodules of calcium phosphate which occur abundantly in the gault of the Ardennes, by smelting them in a blast-furnace with iron. The phosphide thus obtained resembled that just described in its metallic aspect and state of crystalline aggregation, and was also strongly magnetic; its crystalline form, however, was not determined.

According to C. Freese (*Deut. Chem. Ges. Ber.* v. 604) the method employed by Sidot does not yield a definite product, but a mixture of phosphides of variable composition.

**Tetranickelous Phosphide**,  $\text{Ni}_4\text{P}_2$ , is best prepared by treating a nickel-solution with phosphoretted hydrogen in the manner above described. The black precipitate, purified in the same manner as the ferrous compound, gave by analysis (mean) 78.50 p.c. nickel and 20.50 phosphorus, the formula  $\text{Ni}_4\text{P}_2$  requiring 79.19 Ni and 20.81 P. When precipitated nickel hydrate was used in the preparation, a partially oxidised product was obtained, the oxygen being apparently derived from water retained by the hydrate.

Tetranickelous phosphide is not magnetic. It dissolves slowly in dilute hydrochloric acid, quickly in dilute nitric acid; towards strong nitric acid it behaves like iron. In sulphuric acid, and in a mixture of nitric and hydrochloric acids, it dissolves sometimes slowly, sometimes quickly (Schenk, *Chem. Soc. J.* [2], xii. 214).

**PHOSPHINES.** *Phosphine or Gaseous Hydrogen Phosphide*,  $\text{PH}_3$ .—The ordinary method of obtaining this gas by heating phosphorus with aqueous potash gives a mixture of phosphine with hydrogen, the amount of the former varying from 16 to 35 p.c. Better results are obtained with alcoholic potash, but the gas thus produced is still far from pure.

Calcium phosphide, treated with water, gives off a much purer gas, containing only about 13 p.c. of hydrogen; and when hydrochloric acid is substituted for the water, the evolved gas contains about 7 p.c. of hydrogen. The phosphoretted hydrogen obtained from crystallised phosphorous acid contains about 6 p.c. of hydrogen. Perfectly pure phosphine may, however, be obtained by the action of water, or, better, of potash, on the iodide of phosphonium.

This substance, in pieces about the size of peas, is placed in a flask provided with a delivery-tube, and with a bulb-tube having a stopcock passing through the cork in the usual manner. The bulb is filled with potash-solution of about the strength used in combustions, and when the gas is required a few drops are allowed to enter the tube. In this way the evolution can be easily stopped at any desired moment; 7.3 grams of phosphonium-iodide yield about a litre of gas. The gas thus obtained is perfectly pure if collected when free from air; it is entirely absorbed by a solution of chloride of lime; it is not spontaneously inflammable, although, on account of its purity, it is more easily ignited than the impure gas containing hydrogen, which has been deprived of its spontaneous inflammability. According to Rammelsberg, however (*Deut. Chem. Ges. Ber.* vi. 88), it sometimes takes fire spontaneously. When brought in contact with acid of fuming nitric acid it takes fire, as it also does in contact with chlorine or bromine water; by passing the gas through nitric acid containing a trace of nitrous acid, it becomes spontaneously inflammable. On passing a series of electric sparks through the gas, it splits up into its components almost as easily as ammonia does (A. W. Hofmann, *ibid.* iv. 200).

The decomposition of phosphine is also effected, though not completely, by the silent electric discharge. The gas first becomes spontaneously inflammable, and then deposits the solid phosphide of hydrogen. After removing the undecomposed phosphine by absorption, the further action of the discharge splits up the solid phosphide into phosphine and red phosphorus. The latter, being a conductor, causes the silent discharge to change into the spark, and stops the action.

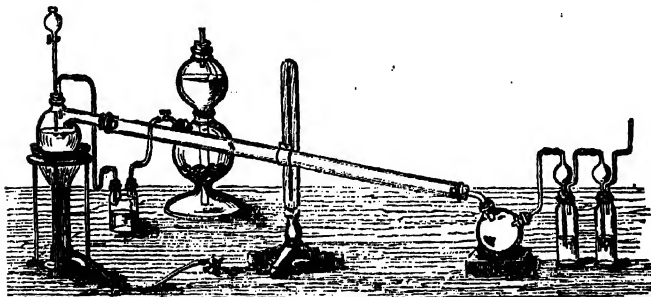
A mixture of phosphine and ethylene yields one of the phosphorus bases, various complicated secondary reactions going on at the same time (P. a. A. Thénard, *Compt. rend.* lxxvi. 1508).

**Phosphine Hydriodide, or Phosphonium Iodide**,  $\text{PH}_3\text{HI}$  or  $\text{PH}_4\text{I}$ .—This compound is now largely applied in the laboratory as a powerful reducing agent, and for the preparation of highly concentrated hydriodic acid, phosphoretted hydrogen,

and the alcoholic phosphines. The following method of preparing it in quantity is given by Hofmann (*Deut. Chem. Ges. Ber.* vi. 291):—

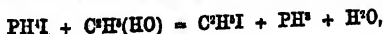
Phosphorus (400 grams) is dissolved in its own weight of carbon sulphide in a retort of 1 litre capacity, and to this solution, kept cool, iodine (680 grams) is added by small portions. The carbon sulphide is then carefully distilled off in a water-bath, an operation which takes 9 or 10 hours. The retort (fig. 25) is then connected with a long wide condensing-tube, and a two-necked globular receiver, from which a connecting tube passes to two condensing-bottles, the first containing weak hydriodic acid, the second water. Heat is then applied to the retort, gently at first, and water (240

Fig. 25.



grams) is slowly added through the drop-funnel. Phosphonium iodide and hydriodic acid are then produced, the latter passing off and collecting in the condensing-bottles, while the former sublimes and collects as a crust, chiefly in the tube, and in smaller quantity in the globular receiver, which, to prevent stoppage, should be connected with the long tube by a wide tube. To prevent the liquid in the condensing-bottles from being forced back, in consequence of the rapid absorption, a slow stream of carbonic acid gas is passed through the apparatus during the whole operation, the first condensing-bottle is charged with dilute hydriodic acid instead of with water, and the tubes connecting these bottles are blown out into bulbs of considerable diameter. A well-conducted sublimation may be completed in 8 or 9 hours. When it is finished, one end of the long condensing-tube is closed with a cork, and the phosphonium iodide, adhering in thick crusts to its inner surface, is detached by means of a stout wire bent and sharpened at the end. The hydriodic acid obtained as a bye-product is moderately strong, but contains a little phosphoric acid.

**Ethyl Phosphines.** Hofmann (*Deut. Chem. Ges. Ber.* iv. 205) has obtained triethyl phosphine by the action of hydrogen phosphide on ethyl iodide under pressure. When phosphonium iodide (10 grams) is introduced into a strong glass tube within which is placed a narrower tube containing three times the quantity of ethyl iodide and a little water, and the sealed tube is heated in the horizontal position to  $160^{\circ}$ – $180^{\circ}$  for several hours, triethyl-phosphine is formed, but in very small quantity. If, however, the tube be charged with 1 mol. phosphonium iodide and 3 mols. alcohol and heated to  $180^{\circ}$ , the contents solidify on cooling to a splendid snow-white crystalline mass consisting of nearly equal parts of the iodides of triethyl- and tetraethyl-phosphonium. The phosphonium iodide and the alcohol first form ethyl iodide and hydrogen phosphide, and these bodies react on one another in the manner just stated:



and—



A similar reaction takes place very easily with methyl alcohol. Allyl alcohol, phenol, and glycerin are also strongly attacked by the phosphonium iodide. This reaction does not yield primary or secondary phosphines.

Drechsel and Finkelstein (*ibid.* iv. 352) have obtained triethyl phosphonium iodide by the action of ethyl iodide on a zinc phosphide, probably  $\text{ZnHP}$ , prepared by passing dry hydrogen phosphide into a well-cooled ethereal solution of pure zinc-ethyl. This compound, which contains 17.80 p.c. phosphorus, is a white friable substance, small.

ing of hydrogen phosphide. Heated to  $150^{\circ}$  in a sealed tube with 5 pts. of ethyl iodide and excess of ether, it yields, together with zinc iodide, a compound of that body with the iodide of triethyl phosphonium, having the composition  $\text{ZnI}^2 \cdot 2(\text{C}^2\text{H}^5)^3\text{HPI}$ .

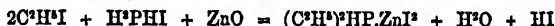
When a mixture of hydrogen phosphide and vapour of methyl iodide was passed over platinum sponge, no combination took place; but when iodide of ethyl or methyl saturated with the gas was left to itself for some time, or heated to  $100^{\circ}$  in sealed tubes, combination was effected. No phosphonium iodide was, however, produced, as the resulting crystals dissolved easily in water without evolution of gas: hence Drechsel and Finkelstein conclude that the iodide of monomethyl- or monethyl-phosphonium was formed by the above reaction. They also state that crystals of monomethyl-phosphonium iodide,  $\text{PH}^3(\text{CH}^3)\text{I}$ , are obtained by heating a mixture of 1 vol. methyl iodide with 1 vol. of a saturated ethereal solution of zinc iodide which has been saturated at  $-10^{\circ}$  with hydrogen phosphide.

Hofmann (*ibid.*, iv. 372), on repeating the experiments of Drechsel and Finkelstein, finds that the reactions described by these chemists yield no primary or secondary but only tertiary phosphines; moreover that the primary and secondary bases are not formed by the action of alcohol on ethyl iodide in any proportions whatever. They are, however, easily produced by heating phosphonium iodide with ethyl iodide in presence of a metallic oxide, such as zinc oxide, the ordinary zinc-white of commerce answering the purpose very well. The best proportions are 1 mol. zinc oxide to 2 mols. phosphonium iodide and 2 mols. ethyl iodide. A mixture of 1 pt. by weight of zinc-white, 4 pts. phosphonium iodide and 4 pts. ethyl iodide is digested in sealed tubes at a temperature not exceeding  $150^{\circ}$  for 6 to 8 hours, by which time the tubes are found to be filled with a homogeneous, almost colourless, crystalline mass. A tube of about 60 c.c. capacity may be charged with 40 to 50 grams of the mixture. In filling the tube, it is best first to introduce the phosphonium iodide, then the zinc oxide, and finally the ethyl iodide; thus arranged these bodies do not react at ordinary temperatures, and the tubes may be sealed with safety.

The main product of the reaction is ethyl-phosphonium iodide, which unites with the zinc iodide to form a double salt:



Simultaneously, however, reaction takes place, but to a less extent, between 2 mols. ethyl iodide, 1 mol. phosphonium iodide, and 1 mol. zinc oxide:



with formation of diethyl phosphine, which combines directly with the zinc iodide. A small quantity of phosphonium iodide, therefore, always remains unacted upon. Together with these reactions, others take place, especially when the temperature has risen at all high, which give rise to the formation of permanent gases, perhaps ethylene or even marsh-gas. In these cases the product is no longer pure white, but has more or less of a reddish-yellow colour, in consequence of the separation of phosphorus iodide; the escaping gases then take fire only momentarily, whereas, when hydrogen phosphide is present, they burn for some minutes.

It is worthy of note that the reaction above described gives rise to the primary and secondary phosphines *only*; and since, as far as has been observed, the same appears to hold good in the methyl series, it follows that the reaction of phosphonium iodide on the iodides of the radicles is complementary to its action on the alcohols, in which case, as above stated, the tertiary and quaternary bodies only are formed.

The separation and purification of the two phosphines present in the product of the reaction is easily accomplished, and is based on the fact that the salts of the primary phosphines are perfectly decomposed by water, in the same manner as phosphonium iodide, with liberation of the phosphine and solution of the acid; whereas, the salts of the secondary phosphines withstand the action of even a large excess of boiling water, but are readily decomposed by alkalis. The operation is as follows:—The product from several tubes being placed in a suitable apparatus from which the air is expelled by a current of hydrogen, is acted on by a slow stream of water, which has been previously boiled and again cooled; the monethyl-phosphine is thus set free and condensed in a spiral surrounded by ice. As some quantity of the extremely volatile phosphine is liable to be carried away by the hydrogen, the gas is caused to pass, before its entry into the atmosphere, through a column of concentrated hydriodic acid. During the operation, this liquid becomes gradually filled with magnificent, dazzling white crystals of pure ethyl-phosphonium iodide. When, by the further addition of water, no more monethyl phosphine is evolved, even on warming, strong caustic soda-solution is added, the operation being still carried on in a current of hydrogen. The diethyl-phosphine then distils over readily on heating, and may be condensed in the ordinary manner.



The liquid thus obtained, after drying over potassium hydrate, is the chemically pure diethyl-phosphine.

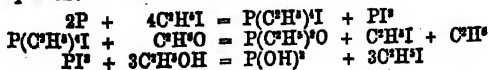
*Monethyl Phosphine*,  $P \begin{pmatrix} C^2H^5 \\ H \\ H \end{pmatrix}$ , is a mobile, colourless, transparent liquid, boiling at  $25^\circ$ ; lighter than and insoluble in water; refracting light strongly, and entirely without action on vegetable colouring matters. It has a most overpowering odour, resembling that of the formonitrils; and, similarly, its vapour produces on the tongue an intensely bitter taste which extends far down the throat. Its fumes bleach cork, like chlorine; caoutchouc is affected by it in a remarkable manner, becoming transparent and losing its elasticity. In contact with chlorine, bromine, or fuming nitric acid, it takes fire. Sulphur and carbon bisulphide combine directly with it, but the resulting bodies are liquid, and not crystalline, like the corresponding triethyl-phosphine derivatives. Concentrated hydrochloric, hydrobromic, and hydriodic acid unite with it to form salts; the solution of the hydrochloride yields with platinum tetrachloride a double salt, crystallising in magnificent carmine-red needles, much resembling freshly prepared chromic anhydride. The *hydriodide*,  $C^2H^5H^2P.HI$ , forms white quadrilateral plates, which may be sublimed unchanged in a current of hydrogen at the temperature of boiling water; the crystals are permanent in dry air. It dissolves in water with complete decomposition; also in alcohol, but with partial decomposition; in ether it is insoluble; concentrated hydriodic acid is the only solvent which dissolves it, though sparingly, unchanged, the addition of ether causing the separation of the salt in large, well-formed plates, often a centimeter in diameter, but of extreme thinness.

*Diethyl Phosphine*,  $P \begin{pmatrix} C^2H^5 \\ C^2H^5 \\ H \end{pmatrix}$ , is a colourless, transparent, perfectly neutral liquid,

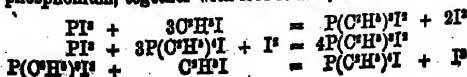
refracting light strongly, lighter than water, and insoluble therein. It boils constantly at  $86^\circ$ , or  $60^\circ$  higher than the primary base. It has a penetrating, persistent odour, different from that of monethyl phosphine, more resembling, although essentially different from, that of triethyl phosphine. It absorbs oxygen with great avidity, combination taking place with great energy, often causing it to take fire on opening the containing vessel. Diethyl phosphine combines both with sulphur and with carbon bisulphide to form liquids, a behaviour which affords a ready means of testing its freedom from admixture of triethyl phosphine. It dissolves easily in all acids, but none of its salts crystallise readily, except the hydriodide. The platinumchloride, which is easily alterable, crystallises in fine, large, orange-yellow prisms. The salts of diethyl phosphine are not decomposed by water.

*Triethyl-phosphine oxide*,  $P(C^2H^5)_3O$ .—Carius (*Ann. Ch. Pharm.* cxxxvii. 117) prepares this compound by acting upon ethyl iodide with phosphorus in sealed tubes at  $160^\circ$ , and heating the product to the same temperature with alcohol. Crafts & Silva (*Chem. Soc. J.* [2], ix. 629) modify this process as follows: 1 pt. of phosphorus is heated to  $175^\circ$  for 24 hours with 13 pts. ethyl iodide in sealed tubes laid horizontally; the crystals, coloured by iodine, which separate on cooling, are melted by gentle heating and transferred to a retort; the residual phosphorus cake (consisting chiefly of amorphous phosphorus) is pulverised, and likewise transferred to the retort; and the whole is boiled with alcohol of 97 p.c. as long as any ethyl iodide distils over. The concentrated solution then deposits white crystals, apparently consisting of compounds of triethyl-phosphine oxide and the hydrate,  $P(C^2H^5)_3OH$ , with iodine and the acids of phosphorus. On-distilling these crystals with 4 pts. of potassium hydrate, triethyl-phosphine oxide is obtained, towards the end of the operation, nearly in the pure state.

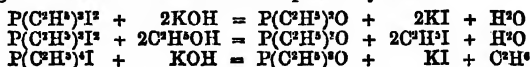
Carius represented the course of the reaction by which this product is obtained, by the following equation:



As, however, the product of the first stage of the reaction is nearly insoluble in water, whereas  $PI^3$  and  $P(C^2H^5)_3I$  are soluble, and moreover not merely the half, but four-fifths of the phosphorus is converted into triethyl-phosphine oxide, Crafts & Silva regard this view as erroneous, and suppose that the reaction represented by the first equation goes further, yielding, as final products, the iodides of triethyl phosphine and tetraethyl-phosphonium, together with free iodine; thus:



In the subsequent decomposition by alcohol and by potash, the greater part of the triethyl-phosphine oxide is produced from the corresponding iodide, inasmuch as the quantity of gas evolved in this reaction is comparatively small:



Triethyl-phosphine oxide boils at  $242^\circ\text{--}243^\circ$  (uncorr.), and crystallises at  $51.9^\circ$ . It is very hygroscopic; traces of water lower its boiling and solidifying points very considerably. It is but slightly volatile with vapour of water. The oxygen in it is very intimately combined, not being either removable or replaceable by sulphur (acting as  $\text{H}^2\text{S}$ ). It likewise offers great resistance to the action of chlorine, no perceptible reaction or formation of hydrochloric acid taking place below  $180^\circ\text{--}200^\circ$ , and the product then formed being decomposed by distillation. Heated to  $190^\circ$  for 4 hours with bromine and a little water, it yields a product which may be distilled, without decomposition, in a vacuum. Hydrochloric acid gas acts upon the oxide with the aid of heat, forming (amongst other compounds containing hydrochloric acid) a substance having nearly the composition  $\text{P}(\text{C}^2\text{H}^5)_3\text{O.HCl}$ . This compound forms silky needles like sulphuric anhydride, and solidifies after fusion at  $127.5^\circ$ . By heating the oxide in tubes with hydrobromic acid, a product was obtained which, under a pressure of 2 inches of mercury, boiled almost constantly at  $205^\circ\text{--}210^\circ$ . It contained only 32.17 p.c. bromine, whereas the formula  $\text{P}(\text{C}^2\text{H}^5)_3\text{O.HBr}$  requires 37.21 p.c. After repeated distillation it contained still less bromine. Neither was any product of definite composition obtained by saturation of the anhydrous oxide with hydrobromic acid at  $150^\circ$  (Friedel & Crafts).

**Methyl Phosphines** (Hofmann, *Deut. Chem. Ges. Ber.* iv. 605). These compounds are formed in the same way as the corresponding ethyl-compounds, by heating in closed tubes 2 mols. phosphonium iodide, 2 mols. methyl iodide, and 1 mol. zinc oxide. A solid crystalline mass is thereby obtained, from which the phosphines are isolated by a method similar to that used for the preparation of the ethyl-compounds. The methyl phosphine, which escapes as a gas on adding water to the product of the reaction, is condensed in a flask surrounded by a mixture of ice and calcium chloride. The residue in the flask, which towards the end of the operation has to be heated in order to drive out all the monophosphine, solidifies, on cooling, to a mass of large, beautiful, perfectly white needles, a compound of dimethyl-phosphonium iodide with zinc iodide, from which the base is liberated by adding a solution of caustic soda; it is condensed in a vessel surrounded by ice-water.

**Methyl Phosphine**,  $\text{PH}^2(\text{CH}^3)$ , is a colourless transparent gas, having even a more overpowering smell than ethyl phosphine. By cold or pressure it may be condensed into a liquid lighter than water, which boils at  $-14^\circ$ . It is insoluble in water, sparingly soluble in ether, more freely in alcohol. In contact with air it fumes, being gradually oxidised, but takes fire when gently heated or when brought in contact with chlorine, bromine, or nitric acid. With acids it forms well-defined salts, which are all decomposed by water, and have the remarkable property of bleaching vegetable colours like chlorine. On holding in the gas a strip of litmus-paper partially moistened with water and partly with an acid, only the latter portion is bleached, showing that the free base itself has not this property.

The hydrochloride,  $\text{P}(\text{CH}^3)_2\text{H}^2.\text{ClH}$ , is obtained by mixing equal volumes of hydrochloric acid gas and methyl phosphine; both gases disappear completely, the salt condensing in well-defined four-sided plates. It is so volatile that it volatilises with ether-vapour. Its solution in concentrated hydrochloric acid gives, with platinum chloride, a double salt forming orange-red crystals. The hydriodide,  $\text{PH}^2(\text{CH}^3).\text{HI}$ , is obtained in thick crystals, by passing the gas into highly-concentrated hydriodic acid. By passing the gas into concentrated sulphuric acid, it is absorbed without blackening of the liquid, and set free again on addition of water. The sulphite is an amorphous white mass, obtained by mixing sulphurous acid and methyl phosphine over mercury. Carbonic acid and hydrogen sulphide do not act upon it, but it combines with sulphur, carbon bisulphide, and chlorocarbonic ether.

**Dimethyl Phosphine**,  $\text{PH}(\text{CH}^3)_2$ , is a colourless liquid, lighter than water, and insoluble therein. It boils at  $25^\circ$ , or at the same temperature as its isomeride, ethyl phosphine,  $\text{PH}^2\text{C}^2\text{H}^5$ . It takes fire at once in contact with air, burning with a bright phosphorus flame. Its salts are all very soluble; the hydrochloride forms with platinum chloride a well-crystallised double salt. It also combines with sulphur and carbon bisulphide.

**Isopropyl Phosphines** (Hofmann, *Deut. Chem. Ges. Ber.* vi. 292). These bases are obtained by heating the corresponding iodides with phosphonium iodide and zinc

oxide to 100° for 5 or 6 hours. The primary and secondary bases are easily separated from one another, like the corresponding methyl- and ethyl-compounds, by treating the hydriodides with water, which decomposes the primary compounds, whereas the secondary hydriodides are decomposed only by alkalis.

**Isopropyl Phosphine**,  $\text{PH}^3(\text{C}^3\text{H}^7)$ , is a light, limpid, very refractive liquid, boiling at 41°, and having a very penetrating odour. It unites with sulphur and with carbon bisulphide, forming uncrystallisable compounds. It readily absorbs oxygen and takes fire on a hot summer day.

**Diisopropyl Phosphine**,  $\text{PH}^2(\text{C}^3\text{H}^7)_2$ , boils at 118°. It absorbs oxygen more quickly than the primary base, a drop placed on filter-paper taking fire and blackening the paper slightly without inflaming it.

**Triisopropyl Phosphine**,  $\text{P}(\text{C}^3\text{H}^7)_3$ , the hydriodide of which is obtained by heating diisopropyl-phosphine with isopropyl iodide to 120°, is a liquid forming a red crystallisable compound with carbon bisulphide. The *hydriodide*,  $\text{P}(\text{C}^3\text{H}^7)_3\text{HI}$ , forms large crystals readily soluble in water and in alcohol, but insoluble in ether.

**Tetrisopropyl-phosphonium iodide**,  $\text{P}(\text{C}^3\text{H}^7)_4\text{I}$ , formed by combining the tertiary base with isopropyl iodide, crystallises from water in cubes or octohedrons.

**Methyl-isopropyl Phosphine**,  $\text{PH}(\text{CH}^3)(\text{C}^3\text{H}^7)$ , is obtained as a hydriodide by heating the primary propyl base with methyl iodide to 100°. The free base boils at 78°-80°.

**Isobutyl Phosphines** (Hofmann, *loc. cit.*) These bases are prepared similarly to the isopropyl-phosphines. *Isobutyl phosphine*,  $\text{PH}^2(\text{C}^4\text{H}^9)$ , boils at 62°; *diisobutyl phosphine*,  $\text{PH}(\text{C}^4\text{H}^9)_2$ , at 153°. Both are oily liquids having the general properties of the phosphines. The secondary base combines with isobutyl iodide at 100°, forming a beautiful crystalline mass of *triisobutyl-phosphine iodide*,  $\text{P}(\text{C}^4\text{H}^9)_3\text{I}$ . Free tri-isobutyl-phosphine boils at 216°; it unites with isobutyl iodide, but the tetrisobutyl-phosphonium iodide has not been obtained in the pure state.

As the tertiary phosphorus-bases and phosphonium-compounds are also produced by heating the alcohols with phosphonium iodide, an attempt was made to prepare the corresponding isobutyl-compounds by heating isobutyl alcohol with phosphonium iodide; but no phosphines were formed, the alcohol being decomposed with formation of hydrocarbons.

**Isopropyl-isobutyl Phosphine**,  $\text{PH}^2(\text{C}^3\text{H}^7)(\text{C}^4\text{H}^9)$ , is formed, as hydriodide, by heating isopropyl phosphine and isobutyl iodide to 130°; it boils at 139°-140°. Heated with ethyl iodide to 100° it yields *ethyl-isopropyl-isobutyl phosphine*, a very oxidisable liquid, boiling at about 190°.

**Methyl-triisobutyl-phosphonium iodide**,  $\text{P}(\text{CH}^3)(\text{C}^4\text{H}^9)_3\text{I}$ . Methyl iodide acts on triisobutyl phosphine with explosive violence. The crystalline product is purified by dissolving it in water, adding an alkali, distilling off the volatile phosphines, then treating the solution with carbonic acid, evaporating to dryness, and exhausting with alcohol. The crystalline residue is readily soluble in water, from which it separates in fine crystals. A very similar body is *methyl-ethyl-isopropyl-isobutyl-phosphonium iodide*, which is obtained by combining methyl iodide with ethyl-isopropyl-isobutyl phosphine.

**Isoamyl Phosphines**,  $\text{PH}^2(\text{C}^5\text{H}^{11})$ . The phosphines of isoamyl (ordinary amyl) are but slowly formed at 100°, but readily at 140°-150°. The primary base boils at 106°-107°, and absorbs oxygen with evolution of heat. *Diisoamyl phosphine*,  $\text{PH}(\text{C}^5\text{H}^{11})_2$ , boils at 210°-215°. A drop placed on litmus paper is oxidised, with formation of dense white phosphorescent fumes, without taking fire. *Triisoamyl phosphine*,  $\text{P}(\text{C}^5\text{H}^{11})_3$ , boils at about 300°, but has not been obtained pure. In one experiment some tetramyl-phosphonium iodide was formed, which, on addition of an alkali, separated as a viscid liquid, but became crystalline on standing for some months.

**Triisoamyl-phosphine oxide**,  $\text{P}(\text{C}^5\text{H}^{11})_3\text{O}$ , is always formed in small quantity in the preparation of triisoamyl phosphine. It boils above 360°, and solidifies, after the phosphine has distilled over, in the neck of the retort, to a crystalline mass which melts at 60°-65°. Water precipitates it from an alcoholic solution as a crystalline powder (Hofmann, *ibid.* vi. 301).

When amyl alcohol and phosphonium iodide are heated to 150°, they yield amyl iodide and hydrogen phosphide, whilst at 170°-180° gaseous hydrocarbons are formed.

**Benzyl Phosphines** (Hofmann, *ibid.* v. 100). These compounds are easily formed by heating crude benzyl chloride with phosphonium iodide and zinc oxide. On distilling the product with steam, a heavy oil passes over, being a mixture of benzyl phosphine and regenerated toluene, which are separated by fractional distillation.

**Benzyl Phosphine**,  $\text{PH}^2(\text{C}^6\text{H}^5)$ , boils at 180°. In contact with the air it quickly takes up oxygen, thick white fumes being formed and the temperature rising 100° or

more. The *hydriodide* is crystalline and is decomposed by water. The *hydrobromide* and *hydrochloride* do not crystallise; the latter forms a yellow precipitate with platinum chloride.

*Dibenzyl Phosphine*,  $\text{PH}(\text{C}^6\text{H}_5)_2$ , is formed, together with the primary base, and remains behind on distillation. It crystallises from alcohol in large, scentless, and tasteless needles, grouped in stars or fascicles; they melt at  $206^\circ$  and volatilise, with partial decomposition, at a higher temperature. It is insoluble in all acids, permanent in the air, even at rather high temperatures.

The aromatic phosphines, analogous to aniline and toluidine, have not yet been obtained.

#### *Formation of Phosphines by the aid of Reduction-Processes.*

The *phosphines of polygenic radicles* cannot be obtained by the same reaction as that by which the phosphines of monatomic radicles are prepared, on account of the reducing action of hydriodic acid. Zinc oxide and phosphonium iodide act on ethylene dibromide at  $160^\circ$ , yielding however nothing but ethyl phosphine. Chloroform is acted on at  $100^\circ$ , but the product is only methyl phosphine. Benzylene chloride,  $\text{C}^6\text{H}_4\text{CHCl}_2$ , and the chloride,  $\text{C}^6\text{H}_5\text{CCl}_2$ , yield only the phosphines of benzyl, which therefore can be readily obtained pure by employing the crude product of the action of chlorine on boiling toluene. For the same reasons crude isopropyl iodide containing allyl iodide yield pure isopropyl phosphine (Hofmann, *ibid.* v. 301).

**PHOSPHINIC ACIDS** (Hofmann, *ibid.* v. 104; vi. 303). These acids are formed from the primary and secondary phosphines by fixation of 3 and 2 atoms of oxygen respectively, and may be regarded as orthophosphoric acid,  $\text{PO}(\text{OH})_3$ , in which one or more of the groups OH is replaced by an alcohol-radicle. They are prepared by treating the corresponding phosphines with nitric acid. The complete oxidation of the phosphorus to phosphoric acid takes place only when the phosphines are heated with the strongest nitric acid, and at very high temperatures.

*Methyl-phosphinic acid*,  $\text{PH}^2(\text{CH}_3)_2\text{O}^2$ , or  $\text{PO}(\text{HO})(\text{CH}_3)$ , is formed by passing gaseous methyl phosphine, evolved on treating with water the crude product of the action of methyl iodide on phosphonium iodide and zinc oxide, into fuming nitric acid. To purify it from a small quantity of phosphoric acid formed at the same time, from phosphoretted hydrogen present in the gas, the nitric acid solution is evaporated on a water-bath, and the residue is dissolved in water and treated with lead oxide, which gives a salt insoluble in water but soluble in acetic acid. The acetic solution filtered from the insoluble phosphate, and freed from lead by hydrogen sulphide, leaves on evaporation an oily liquid which solidifies on cooling to a white mass resembling spermaceti. This substance is methyl-phosphinic acid; it is easily soluble in water, reddens litmus paper, and has an agreeable acid taste. It also dissolves in alcohol, and to a smaller extent in ether. It is remarkably stable, not being acted upon by fuming nitric acid, or even by evaporation with aqua regia. It melts at  $105^\circ$ , and volatilises in great part without decomposition. It is isomeric with methyl-phosphorous acid, but differs greatly in its properties from that compound, which is uncrystallisable, and is resolved at a gentle heat into phosphorous acid and methyl alcohol.

Methyl-phosphinic acid forms two classes of salts,  $\text{PHR}(\text{CH}_3)_2\text{O}^2$  and  $\text{PR}^2(\text{CH}_3)_2\text{O}^2$ , the former having an acid, the latter an alkaline reaction. The alkali salts are soluble and only slightly crystalline; the ammonia salt loses ammonia on evaporation, and leaves the acid. Many of the heavy metallic salts are insoluble or dissolve with difficulty.

The primary or *monargentate salt*,  $\text{PHAg}(\text{CH}_3)_2\text{O}^2$ , crystallises in white needles, and is easily resolved by water, or even by alcohol, into the free acid and the secondary or *diargentate salt*,  $\text{PAg}^2(\text{CH}_3)_2\text{O}^2$ , which is a white insoluble powder. The *primary lead salt* is also decomposed by water; the *secondary lead salt*,  $\text{P}(\text{CH}_3)_2\text{PbO}^2$ , is easily obtained pure as a white precipitate, almost insoluble in water, but soluble in acetic acid. The *primary barium salt*,  $\text{P}^2(\text{CH}_3)_2\text{H}^2\text{BaO}^2$ , is obtained in white microscopic needles by adding alcohol to its concentrated aqueous solution, or as a gummy mass.

*Dimethyl-phosphinic acid*,  $\text{PH}(\text{CH}_3)_2\text{O}^2 = \text{PO}(\text{OH})(\text{CH}_3)$ , is obtained by mixing a solution of dimethyl phosphine in hydrochloric acid with fuming nitric acid, and, after the reaction is over, evaporating the liquid, saturating with silver oxide, and treating the solution of the silver salt with hydrogen sulphide. On evaporating the resulting acid solution, dimethyl-phosphinic acid is obtained as a white crystalline mass, becoming slightly brown in contact with the air. It is very soluble in water, alcohol, and ether, the solutions having an acid reaction. The crystals melt at  $70^\circ$ , volatilise without decomposition at a higher temperature, and the distilled product exhibits an unchanged melting point.

Dimethyl-phosphinic acid forms only one series of salts, having the composition

$P(CH^3)_3RO^3$ . The *silver salt*,  $P(CH^3)_3AgO^3$ , forms white needles extraordinarily soluble in water, but very slightly soluble in absolute alcohol and ether. The barium and lead salts are neutral, very soluble, uncrystallisable compounds.

*Methyl-phosphinic chloride*,  $P(CH^3)_2OCl^2$ , is obtained by the action of phosphorus pentachloride on methyl-phosphinic acid. It is a crystalline solid, melting at  $32^\circ$  and boiling at  $183^\circ$ . Water, alcohol, ammonia, and aniline, act violently on it as on other acid chlorides.

*Dimethyl-phosphinic chloride*,  $P(CH^3)_2OCl$ , melts at  $66^\circ$  and boils at  $204^\circ$ . Water and alcohol decompose it, but with less violence than the preceding compound.

*Ethyl-phosphinic acid*,  $P(C^2H^5)_2H^3O^3$ , is prepared like the corresponding methyl-compound, which it resembles in appearance and many of its properties. It melts at  $44^\circ$ . Its *silver salt* is an amorphous yellowish powder, insoluble in water and in alcohol.

*Diethyl-phosphinic acid* has not been obtained in the crystalline state, but only as a liquid which does not solidify at  $-25^\circ$ . The *silver salt*,  $P(C^2H^5)_2AgO^3$ , is crystalline.

*Isopropyl-phosphinic acid*,  $P(C^3H^7)_2HO^3$ , prepared like the corresponding ethyl- and methyl-compounds, is a white mass resembling paraffin, and melting between  $60^\circ$  and  $70^\circ$ ; it dissolves in water, and more freely in alcohol.

*Isobutyl-phosphinic acid* is a very similar body, melting at  $100^\circ$ .

*Amyl-phosphinic acid*,  $P(C^5H^{11})_2HO^3$ , is prepared by adding amyl phosphino to a mixture of equal volumes of fuming nitric acid and nitric acid of sp. gr. 1.2; the fuming acid alone acts too violently and sets fire to the base. The acid crystallises from hot water in small pearly rhombic plates melting at  $160^\circ$ . The silver salts of this acid and of the two acids last described are white amorphous precipitates.

The secondary phosphines of isopropyl, isobutyl, and amyl, yield, by oxidation with nitric acid, the corresponding phosphinic acids, which, however, have not yet been obtained in a state fit for analysis; neither have any of their salts been prepared in the pure state. The free acids are oily liquids insoluble in water.

**PHOSPHOCHROMITE.** This name is given by R. Hermann (*J. pr. Chem.* [2], i. 449) to a mineral from Beresovsk in Siberia, hitherto regarded as rauquelinite, to which he assigns the formula  $3(2CuO.P^2O^3) + 5(3PbO.CrO^3) + 3H^2O$ . Implanted in listwaenite, and accompanied by lead chromate and pyromorphite, it forms a nodular aggregate exhibiting small crystals on its surface (thin laminae with rounded end-faces). Blackish-green; yields a siskin-green powder. Hardness = 3; sp. gr. = 5.80. Analysis gave:

PbO	CaO	FeO	CrO <sup>3</sup>	P <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O
68.33	7.36	2.80	10.13	9.94	1.16 = 99.72.

**PHOSPHOPLATINUM COMPOUNDS.** See PLATINUM (p. 987).

**PHOSPHORITE.** See PHOSPHATES (pp. 969, 974).

**PHOSPHORUS.** *Quantivalence.*—Wicholhaus (*Ann. Ch. Pharm., Suppl.* vi. 257); *Jahresb. f. Chem.* 1868, 148) regards phosphorus as a trivalent element, founding his opinion mainly on the action of chlorine on ethyl-phosphorous chloride and that of phosphorus bromochloride on benzoic acid. Geuther u. Michaelis, however (*Jenaische Zeitschrift*, vi. 242; *Jahresb.* 1870, 276), have shown that these reactions may be better explained on the generally received view that the maximum quantivalence of phosphorus is 5.

*Allotropic modifications: Black Phosphorus.*—This modification, originally obtained by Blondlot, by the sudden cooling of melted phosphorus (iv. 503), may also be produced by distilling ordinary phosphorus with a trace of mercury, or by heating it to  $100^\circ$  for several hours with mercury under water. The product obtained by either of these two methods is not homogeneous, but owes its colour to a large number of black specks more or less irregularly distributed; on fusion, these specks disappear, and the phosphorus turns white, resuming its black colour, however, on cooling. On treating the phosphorus with carbon sulphide, this black matter remains undissolved in extremely small quantity. The quantity of it does not appear to be increased either by prolonged contact of the phosphorus with the mercury, or by the quantity of the latter present. By repeated distillation, whereupon the black substance passes over first, a product may be obtained free from mercury (*Compt. rend.* lxx. 856).

*Conversion of Ordinary into Red Phosphorus in Sunshine.*—Phosphorus dissolved in carbon sulphide behaves like sulphur when exposed to sunshine. Where the sun's rays fall upon it, a yellow spot of amorphous phosphorus is formed, quickly changing to brown-red; the action is, however, less energetic than in the case of sulphur, and requires a longer time. The transmitted light contains all the luminous rays, the light being merely fainter near the line H. The least refrangible of the chemical

rays may still be detected by their effect on phosphorescent bodies; but beyond N all the chemical rays have disappeared (A. Lallemand, *Compt. rend.* lxx. 182).

**Reciprocal Transformation of Ordinary and Red Phosphorus.**—The conditions of these transformations have been investigated by G. Lemoine (*Compt. rend.* lxxiii. 797, 837, and 990; *Chem. Soc. J.* [2], ix. 1167). The experiments were made at the boiling point of sulphur (440°) in Deville's apparatus (v. 373). The flasks (of 60 to 600 c.c. capacity) were exhausted of air after the introduction of the phosphorus, then closed and heated in every part to 440°; then, after a certain time, they were very quickly cooled with warm water, to avoid the occurrence of intermediate temperatures; the two modifications of phosphorus were separated by carbon sulphide and their quantities determined. From a large number of experiments Lemoine concludes that the conversion of ordinary into red and of red into ordinary phosphorus is essentially dependent on vapour tension. The conversion is never complete, but its rapidity depends in a great measure on the quantity of phosphorus originally present, and diminishes the more nearly a certain limit of transformation is approached. In fact, whichever of the two allotropic modifications is operated on, the transformation always tends towards the same limit, viz., the production of about 3.6 grams of ordinary phosphorus per litre of space.

According to Troost & Hautefeuille (*Compt. rend.* lxxvi. 76, 219; *Chem. Soc. J.* [2], xi. 599), the transformation of ordinary into red phosphorus, like that of cyanic acid into cyamelide (1st Suppl. 518), obeys different laws accordingly as the phosphorus is in the liquid or the vaporous state. The liquid element, at 280° for instance, is analogous to liquid cyanic acid, being wholly transformed into red phosphorus. The vapour given off at 260° is stable; but that formed at higher temperatures is slowly and partially converted into red phosphorus, the production of which ceases when the tension has attained a given minimum; the rapidity with which this change is effected is greater the higher the temperature.

**Luminosity of Phosphorus.**—W. Müller (*Pogg. Ann.* cxli. 95) finds, in accordance with earlier observations (iv. 503), that phosphorus is not oxidised, and does not shine in pure oxygen under ordinary atmospheric pressure, but that on rarifying the oxygen, either by means of the air-pump, or by admixture of foreign gases, the phosphorus shines at ordinary temperatures, and at a lower temperature the greater the dilution of the gas. Oxidation begins at 10°–11°, when the oxygen is expanded by about  $\frac{1}{2}$  of its original volume, or at 17.5° when 1 vol. nitrogen is added to every 1.5 vol. oxygen, or at 16° when an equal volume of hydrogen is added. The volatilisation of the phosphorus is not interrupted by the presence of substances which destroy the luminosity. Phosphorus is slightly soluble in water, and when bubbles of hydrogen containing air are passed through such phosphoretted water (filtered), they shine with a bright light.

**Reaction with Ammonia.**—According to Blondlot (*Compt. rend.* lvi. 1250), phosphorus left for a long time in contact with excess of aqueous ammonia in closed vessels is converted into a black friable substance which, on exposure to the air, turns yellow and gives off a small quantity of ammonia. According to Commaille, on the other hand (*Compt. rend.* lxxiii. 263; *Moniteur Scientifique* [3], i. 701), the product thus obtained is not black but green, and always has the composition  $P^2H$ . When boiled with water, it does not give off any gas, but only a whitish fume, and the water which distils over is alkaline, while that which remains behind has a faint acid reaction. On boiling the compound with sulphuric acid, the phosphorus dissolves, with separation of sulphur and formation of phosphorus trisulphide. Ordinary nitric acid acts strongly on the compound at ordinary temperatures, whereby it is distinguished from ordinary phosphorus and nitrogen phosphide. It differs also from the compound  $P^2H$  in not being set on fire by nitric acid. From a solution of cupric sulphate it throws down phosphide of copper, but not the metal, as is the case with phosphorus and  $P^2H$ . When triturated with potassium chlorate, it explodes violently. It is decomposed by potash, especially when heated, a character which distinguishes it from the compound described by Flückiger (iv. 505).

Phosphorus is not acted on by gaseous ammonia, and very little by a solution of ammonium carbonate; but alcoholic ammonia left for 2½ months in contact with phosphorus produced non-spontaneously inflammable phosphoretted hydrogen gas, the green powder above described, and small crystals, probably consisting of ammonium phosphite or hypophosphite. The alcohol evaporated on the water-bath left a syrupy mass which deposited crystals of unknown composition (Commaille).

**Action of Phosphorus on Metallic Solutions.**—When an ammoniacal solution of copper oxide, nickel oxide, silver oxide, or cadmium oxide is heated with phosphorus and a little benzene in a vessel connected with a reversed condenser, dark precipitates are formed, which may be washed with water, alcohol and carbon sulphide, and dried in vacuum. The copper precipitate consists chiefly of metallic copper and copper oxide.

Nickel gives a black precipitate consisting of a mixture of nickel phosphide and a salt of one of the acids of phosphorus. From the silver solution metallic silver is reduced (Oppenheim, *Deut. Chem. Ges. Ber.* v. 979).

**Reaction with Turpentine Oil.**—When  $\frac{1}{2}$  oz. of phosphorus is gradually added to 2 pounds of ordinary turpentine-oil (containing oxygen) heated to  $40^{\circ}$ , the flask being removed from the sand-bath as soon as the phosphorus melts, and agitated, the liquid on cooling deposits the excess of phosphorus, which quickly turns red, and a white crystalline, spermaceti-like mass consisting of turpentine-phosphorous acid, said to have the composition  $C^{10}H^{16}PO^2$ . This compound has an acid reaction, and is converted, on exposure to the air, into a resinous substance, smelling like pine-resin, in which phosphoric acid can be directly detected. It melts at  $50^{\circ}$ , with decomposition, to a yellow resinous mass, and decomposes in a stream of hydrogen at  $40^{\circ}$ , with evolution of spontaneously inflammable phosphoretted hydrogen. With earths and metallic oxides it forms insoluble salts. The acid is not poisonous; doses of 0.03 to 0.3 gram may be given to dogs and rabbits without any other effect than a lowering of the bodily temperature. Its formation appears to be the cause of the action of turpentine-oil as an antidote to poisoning by phosphorus (Köhler a. Schimpf, *Dingl. pol. J.* cxcix. 510).

#### Haloid Compounds of Phosphorus.

**Chlorides.** 1. **Trichloride or Phosphorous Chloride,  $PCl_3$ .**—**Reactions.**—With Bromine. According to Michaelis (*Deut. Chem. Ges. Ber.* v. 9), phosphorous chloride unites directly with bromine, forming the compound  $PCl_2Br_2$ ; according to Pinnault (*Compt. rend.* lxxiv. 868), the product has the composition  $PCl_2Br^2$  (see CHLOROBROMIDES, p. 961).

2. **With Water.**—The decomposition of phosphorous chloride by water is sometimes attended with separation of phosphorus. From experiments by Kraut (*Ann. Ch. Pharm.* clviii. 333), it appears that when the chloride is added by drops to ice-cold water, with continual stirring, only a trace of phosphorus is obtained; but if the chloride is dropped into boiling water, each addition is attended by a luminous appearance and considerable separation of amorphous phosphorus. The luminous appearance can be avoided by using moderately warm water, when also phosphorus is obtained. When trichloride of phosphorus is distilled with a little water, or, what is the same thing, with phosphorous acid, phosphorus separates in reddish-yellow drops, and the residue contains orthophosphoric acid. The reaction would seem to be as follows:—



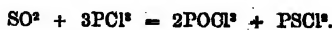
Tribromide of phosphorus behaves with phosphorous acid in a similar way to the trichloride, but the decomposition takes place at a somewhat higher temperature. Geuther (*Jenaische Zeitschr.* vii. 122) finds that, with water at  $80^{\circ}$ , only a very slight deposition of phosphorus takes place; with water which had been boiling for a moment before the experiment, he noticed an appearance near the mouth of the test-tube which contained the water, much resembling phosphorescence, but no phosphorus was separated. By varying the conditions of the experiment, he has been led to conclude that it is only in presence of an excess of air, that the phosphorescent phenomena are exhibited by the phosphorous chloride when dropped into water. He supposes that part of the phosphorous chloride is rendered gaseous; this is decomposed, giving part of the phosphorous chloride is rendered gaseous; this is decomposed, giving hydrochloric acid and phosphorous acid, which, by the excess of oxygen present, is oxidised to phosphoric acid: a small part of the phosphorous acid formed may be reduced to phosphoretted hydrogen, and this again decomposed, giving water and free phosphorus, and hence the small quantity of separated phosphorus.

Distilled with a solution of phosphoric acid, phosphorous chloride gives hydrochloric acid, free phosphorus, and phosphorus oxychloride.

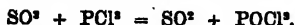
3. **With Anhydrides and Chlorides** (Michaelis, *ibid.* vi. 239; vii. 110). Phosphorous chloride does not exhibit very great affinity for oxygen at ordinary temperatures, but the affinity increases very rapidly with the temperature, so that at high temperatures phosphorous chloride is capable of decomposing very stable compounds; it belongs therefore to the class of reducing agents. When the compound on which it acts contains any element which has a powerful affinity for chlorine, a large quantity of phosphoric acid is produced, with but little oxychloride of phosphorus. Thus most metallic oxides form chlorides and phosphates, with but little phosphorus oxychloride. The only oxide directly reduced to metal by phosphorous chloride is lead oxide. Antimony liberates the phosphorus and is itself converted into trichloride.

Liquid **phosphorous anhydride** mixes with phosphorous chloride at ordinary temperatures without evolution of heat, and the two bodies may be heated together in a sealed tube to  $140^{\circ}$ , without producing any sensible reaction; but when passed together in

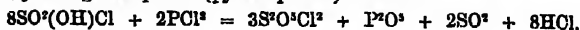
the state of vapour through a red-hot tube, they yield oxychloride and sulphochloride of phosphorus, thus:



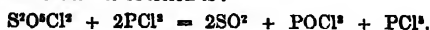
With *sulphuric anhydride*, phosphorous chloride reacts energetically, even when both substances are cooled, the products being sulphurous anhydride and phosphorus oxychloride:



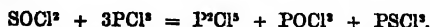
With *sulphuric chlorhydrate* (sulphuryl-hydroxyl chloride) reaction takes place in the cold, yielding disulphuric (pyrosulphuric) chloride:



With *disulphuric chloride* the reaction is:



With *sulphurous chloride* (thionyl chloride) reaction takes place slowly but completely at  $160^\circ$  in sealed tubes, yielding the preceding products, together with phosphorus pentachloride:

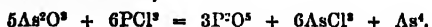


With *sulphur chloride*,  $\text{S}^2\text{Cl}^2$ , the products are pentachloride and sulphochloride of phosphorus, the action being more energetic than in the last case:



This is a convenient way of preparing the sulphochloride.

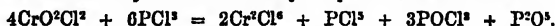
With *arsenious oxide* the reaction,



takes place directly, without previous formation of phosphorus oxychloride.

With *arsenic oxide* no reaction appears to take place even at  $200^\circ$ .

With *chromic oxychloride* a very energetic action takes place, accompanied by a hissing noise and emission of light: hence the phosphorous chloride must be well cooled and the chromic oxychloride added by drops. The reaction is:



The phosphorus pentachloride, however, acts partially on the anhydride, producing an additional quantity of oxychloride:

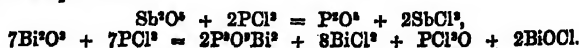


When phosphorous chloride was heated to  $166^\circ$  for two days with *potassium dichromate*, the latter was partly converted into chlorochromate, apparently according to the equation:



With *antimonious oxide* phosphorous chloride yields amorphous phosphorus and antimonious chloride. Now, as arsenious oxide and phosphorous chloride yield phosphoric anhydride, arsenious chloride, and free arsenic (*supra*), it may be supposed that in the present case metallic antimony was first set free and then liberated phosphorus from the chloride; and this view is confirmed by direct experiment. Arsenic and bismuth heated with phosphorous chloride separate only traces of phosphorus. Hence it follows that antimony, at least at high temperatures, has a greater affinity to chlorine than phosphorus, arsenic, or bismuth.

*Antimonic oxide* and *bismuth trioxide* are decomposed by phosphorous chloride according to the equations:



*Lead oxide* and phosphorous chloride do not act on one another at  $160^\circ$ ; but when lead oxide is moistened with phosphorous chloride and heated directly over a lamp, a violent action takes place attended with ignition, and a large quantity of lead is reduced:



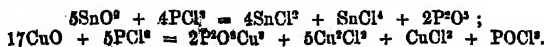
This experiment is very well adapted for exhibiting the reducing action of phosphorous chloride.

*Lead dioxide* acts on heated phosphorous chloride, with ignition, according to the equation:





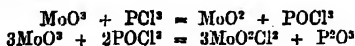
*Stannic oxide* and *cupric oxide* act on phosphorous chloride at 160°, according to the equations:



Cupric oxide, moistened with phosphorous chloride and heated rather strongly over a lamp, is decomposed, according to the above equation, with ignition and appearance of flame.

Precipitated *mercuric oxide* acts on phosphorous chloride even at ordinary temperatures, in exactly the same manner as cupric oxide; the crystallised oxide acts only when heated in a sealed tube to 160°.

*Molybdic trioxide*, in contact with phosphorous chloride, even at ordinary temperatures, becomes heated and acquires a blue colour; on heating the substances together in a sealed tube to 160°, the contents turn brown. The action probably takes place according to the equations:

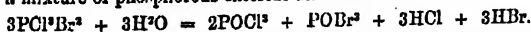


*Tungstic trioxide*, heated with phosphorous chloride even to 200°, merely turns green on the surface without undergoing any further alteration.

*Manganese dioxide* and *ferric oxide* appear also not to be acted on by phosphorous chloride.

**Chlorobromide**,  $\text{PCl}^3\text{Br}^2$  (Michaelis, *Deut. Chem. Ges. Ber.* v. 9). This compound is formed by direct combination of bromine with phosphorous chloride. According to Wichelhaus, the two bodies unite, with evolution of heat, to form a compound which crystallises in a freezing mixture, but separates at ordinary temperatures into two liquid layers; and he considers that the compound is broken up on liquefaction just as  $\text{PCl}^3$  is resolved into  $\text{PCl}^3 + \text{Cl}^2$  when vaporised. Michaelis, on the other hand, finds that it possesses considerable stability, even at ordinary temperatures. The combination takes place but slowly; and when phosphorous chloride and bromine are first mixed, a liquid is obtained consisting of two layers—solutions respectively of phosphorous chloride in bromine, and of bromine in phosphorous chloride. In a freezing mixture at  $-20^\circ$  this liquid solidifies, but separates again into two layers on fusion. If, however, the mixture be allowed to remain undisturbed in a sealed tube at winter temperature for about a week, a crystalline mass is obtained which does not form two layers again at ordinary temperatures, but a homogeneous liquid.

Phosphorus chlorobromide is a yellowish red mass resembling phosphorus pentabromide. At  $35^\circ$  it is resolved into  $\text{PCl}^3$  and  $\text{Br}^2$ . Water has the same action upon it as upon a mixture of phosphorous chloride and bromine:

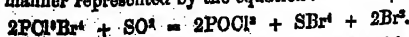


The chlorobromide is decomposed by *sulphur dioxide*, yielding phosphorus oxychloride and sulphur tetrabromide:



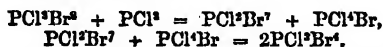
the latter, however, being resolved by distillation into  $\text{SBr}$  and  $\text{Br}^2$  (Michaelis, *Jenaische Zeitschr.* vi. 296).

When a crystal of the compound  $\text{PCl}^3\text{Br}^2$ , or even a portion of the phosphorous chloride which covers these crystals at the time of their formation, is introduced into a mixture of phosphorous chloride and bromine, the lower layer immediately solidifies to a mass consisting of the compound  $\text{PCl}^3\text{Br}^4$ . Michaelis explains the formation of this compound on the supposition that the lower layer of liquid formed on mixing phosphorous chloride with bromine is a supersaturated solution of  $\text{PCl}^3\text{Br}^2$  in bromine. At the moment when crystallisation is set up by the introduction of solid  $\text{PCl}^3\text{Br}^2$ , the latter unites with the excess of bromine and crystallises out with it, just as a salt separates from aqueous solution in combination with water of crystallisation. The compound,  $\text{PCl}^3\text{Br}^4$ , forms large fine crystals having a dark red colour with a blue reflex. When heated it melts to a dark red liquid, which gradually separates into two layers, but on solidification the original crystals reappear. They are decomposed by a large quantity of water into phosphoric, hydrochloric, and hydrobromic acids and free bromine; by a small quantity of water, into chloride and bromide of phosphoryl, hydrochloric and hydrobromic acids, and free bromine. Dry sulphur dioxide decomposes them in the manner represented by the equation:



Bromochlorides of phosphorus, containing still larger quantities of bromine, have been obtained by Prinsault (*Compt. rend.* lxxiv. 368). When bromine is added to

phosphorous chloride till the two layers first formed have disappeared, and the whole is heated in the water-bath to  $65^{\circ}$  as long as bromine continues to escape, there remains a red-brown oily liquid which solidifies, at  $4^{\circ}$  or  $5^{\circ}$  above  $0^{\circ}$ , to brown metallically lustrous needles having the composition  $\text{PCl}^2\text{Br}^2 = \text{PBr}^2.3\text{ClBr}$ . This compound may be distilled without decomposition below  $90^{\circ}$ , and its vapour is colourless. By rapid distillation above  $90^{\circ}$  it is decomposed, yielding the compound  $\text{PCl}^2\text{Br}$ , which collects in the receiver in fine prismatic crystals. This last compound is also formed when phosphorous chloride is dropped into bromine till two layers of liquid are formed. Fine crystals then form after a while, sometimes 2 or 3 mm. long. These crystals dissolve in phosphorous chloride at ordinary temperatures, and, on heating the solution to the boiling point of the chloride, yellow crystals are deposited consisting of the compound  $\text{PCl}^2\text{Br}$  or  $\text{PCl}^2.\text{ClBr}$ , which is also produced by the action of bromine chloride on phosphorous chloride. By means of this compound Prinvaalt has obtained the tetrabrominated compound,  $\text{PCl}^2\text{Br}^4$ , already described, the formation of which may perhaps be represented by the equations:



Michaelis (*Deut. Chem. Ges. Ber.* v. 414) has repeated Prinvaalt's experiments with somewhat different results. By adding bromine in excess to phosphorous chloride, so that about 4 mols. bromine should be present for every 1 mol.  $\text{PCl}^2$ , he obtained, with somewhat considerable rise of temperature, a uniform oily liquid which, after a few minutes, began to deposit a large quantity of crystals, and solidified completely after about two hours. These crystals were brown needles with a beautiful green metallic reflex, but so unstable that they could not be completely separated from the mother-liquor. They had nearly the composition  $\text{PCl}^2\text{Br}^2$ , and melted at about  $25^{\circ}$ , the liquefied mass solidifying again completely on cooling. At temperatures below  $90^{\circ}$  its vapour is not colourless, but has the colour of bromine-vapour.

Prinvaalt regards the compounds above described as compounds of phosphorus pentabromide with bromine chloride,  $\text{ClBr}$ . On this view the action of sulphur dioxide upon them should give rise to phosphoryl tribromide,  $\text{POBr}^3$ , and bromine chloride; this, however, is not the case, the actual products being phosphoryl trichloride, sulphur bromide, and free bromine. This makes it probable that the bodies in question are additive compounds of bromine with  $\text{PCl}^2\text{Br}^2$ , namely  $\text{PCl}^2\text{Br}^2.\text{Br}^2$ , and  $\text{PCl}^2\text{Br}^2.3\text{Br}^2$ , analogous in constitution to  $\text{PCl}^2.\text{ICl}$ ,  $\text{PCl}^2.\text{FeCl}^2$ , &c. (Michaelis).

**Oxychlorides.** *Phosphoryl Trichloride*,  $\text{POCl}^3$ .—This compound, cooled down to  $-10^{\circ}$ , remains liquid even when shaken, but when touched with a solid body, such as the end of a glass rod, it immediately solidifies to a crystalline mass. The long, colourless, leaf-like crystals melt at  $-1.5^{\circ}$ . Below this temperature they are permanent, and will lie upon ice for some time without decomposing. A small crystal is sufficient to cause a considerable quantity of the liquid oxychloride, cooled to  $-2^{\circ}$ , to solidify completely (Geuther a. Michaelis, *Deut. Chem. Ges. Ber.* iv. 769). According to Thorpe (*Chem. Soc. J.* [2] ix. 1162), the melting point of this compound is  $+2.5^{\circ}$ .

Phosphoryl trichloride unites very easily with boron trichloride, forming the compound  $\text{PBOCl}^3 = \text{POCl}^3 + \text{BCl}^3$ , which, however, is completely resolved by sublimation into its components (see Boron, p. 207).

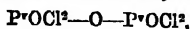
*Phosphoryl bromodichloride*,  $\text{POBrCl}^2$ , solidifies at  $0^{\circ}$  to large colourless crystals which liquefy at  $+11^{\circ}$ . The crystals of this compound appear to be isomorphous with those of the trichloride and tribromide of phosphoryl (Geuther a. Michaelis).

**Pyrophosphoryl Chloride**,  $\text{P}^2\text{O}^2\text{Cl}^4$  (Geuther a. Michaelis, *Deut. Chem. Ges. Ber.* iv. 766).—This compound, the analogue of pyrophosphoric acid,  $\text{P}^2\text{O}^2(\text{OH})^4$ , is formed, together with phosphoryl chloride, by the action of nitrogen tetroxide on tetroxide on cooled phosphorous chloride. The best way of preparing it is to allow the vapours of the liquefied tetroxide (prepared from lead nitrate) to pass into phosphorous trichloride cooled by a freezing mixture (20 grams  $\text{NO}^2$  to 100 grams  $\text{PCl}^3$ ). The reaction commences immediately, with evolution of nitrogen, nitrogen dioxide, and vapours of nitrosyl monochloride ( $\text{NOCl}$ ). The phosphorus trichloride becomes redened by the presence of the last-mentioned compound, and phosphorus pentoxide separates out. When the whole of the nitrogen tetroxide has been added, the freezing mixture is replaced by lukewarm water in order to distil off the nitrosyl chloride. The liquid remaining is then rectified. Much unattacked phosphorus trichloride first passes over, next a considerable amount of phosphoryl trichloride, after which the boiling point rises rapidly to  $200^{\circ}$ , between which temperature and  $230^{\circ}$  the new compound distils over. It is advisable to prepare a large quantity of material by repetitions of the above operation before commencing to rectify. 360 grams of phosphorus

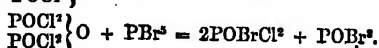
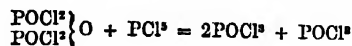
trichloride yielded 232 grams of phosphoryl trichloride, and only 40 grams (11.4 p.c.) of the pyrophosphoryl chloride.

Pyrophosphoryl chloride is a colourless liquid, which boils between 210° and 215°, and decomposes slightly on distillation into phosphoryl trichloride and phosphorus pentoxide:  $3P^2O^2Cl^4 = 4POCl^3 + P^2O^5$ . It fumes in the air and carbonises corks. Its specific gravity is 1.58 at 7°. It does not solidify at -18° on contact with a solid body. It is immediately decomposed by water, producing hydrochloric and ordinary phosphoric acid.

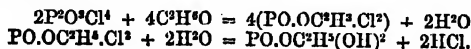
The constitution of pyrophosphoryl chloride may be represented by the formula:



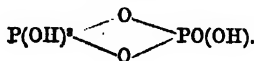
the two univalent groups  $POCl^2$  being held together by an atom of bivalent oxygen. This view of its constitution is confirmed by its reactions with pentachloride and pentabromide of phosphorus, with the former of which it yields 3 mols. phosphoryl trichloride, and with the latter 2 mols. phosphoryl bromodichloride and 1 mol. phosphoryl bromide:



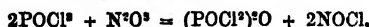
With *alcohol*, pyrophosphoryl chloride yields ethyl-phosphoric chloride, a portion of which is decomposed by the water simultaneously formed, into ethyl-phosphoric acid and hydrochloric acid:



As pyrophosphoryl chloride when decomposed by water yields, not pyrophosphoric but orthophosphoric acid, the former acid should perhaps be represented, not by the formula  $PO(OH)^2-O-PO(OH)^2$ , but by the unsymmetrical formula:



Attempts were made to obtain pyrophosphoryl chloride by the action of nitrous acid on phosphoryl chloride, according to the equation:



also by the very gradual action of phosphorus pentoxide on the pentachloride; but in both cases only with negative result.

The preparation of pyrophosphoryl bromide by the action of  $N^2O^4$  or  $N^2O^3$  on  $PBr^3$  was likewise unsuccessful, the products consisting merely of ordinary phosphoryl bromide and phosphorus pentoxide.

Metaphosphoryl chloride,  $PO^2Cl$  (?), Gustavson (*Deut. Chem. Ges. Ber.* iv. 753), by heating equivalent quantities of phosphorus pentoxide and phosphoryl chloride in a sealed tube to 200° for six hours, obtained a very viscid, transparent mass, probably formed according to the equation  $P^2O^3 + POCl^3 = 3PO^2Cl$ .

**Sulphobromides** (Michaelis, *Ann. Ch. Pharm.* clxiv. 9; *Deut. Chem. Ges. Ber.* iv. 777, v. 4).

1. *Pyrophosphoric Sulphabromide*,  $P^2S^2Br^4 = PSBr^2-S-PSBr^2$ .—To prepare this compound, finely-powdered phosphorus trisulphide is moistened with carbon sulphide, and the required quantity of bromine (diluted with about an equal volume of carbon sulphide) is added by drops, with repeated shaking and continued cooling of the vessel. The carbon sulphide is then distilled off, the residual oily product is exhausted with ether, and the clear decanted solution is freed from ether by distillation in a stream of carbonic anhydride at as low a temperature as possible. The sulphobromide then remains as an oily liquid which is often turbid at first, but soon becomes quite clear on standing in a closed vessel.

Pyrophosphoric sulphobromide is a light yellow oily liquid, which in contact with the air fumes strongly and becomes turbid from separation of sulphur. Its odour is aromatic and pungent. Sp. gr. = 2.2621 at 17°. It is decomposed by distillation into pentasulphide and orthosulphobromide of phosphorus:



the ortho-compound being then further resolved into sulphur, and the compound

$P^2Br^2S$ . The orthosulphobromide is also produced by heating the pyrosulphobromide with the pentabromide:

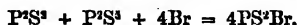


Pyrophosphoric sulphobromide is decomposed by water into sulphur, orthophosphoric sulphobromide, hydrogen sulphide, phosphorus, and a sulphuretted phosphoric acid, probably pyrosulphophosphoric acid,  $P^2S^2(OH)^4$ . The action of alkalis is like that of water, but more violent, and is not attended with separation of sulphur or of orthophosphoric sulphobromide.

With absolute alcohol, pyrophosphoric sulphobromide yields the following ethylated substitution-products.

Triethyl-pyrophosphoric Sulphobromide . . .	$P^2S^2(OC^2H^5)^2Br$
Ethyl Pyrosulphophosphate . . .	$P^2S^2(OC^2H^5)^4$
Diethoxyl-diethylsulphyl-pyrosulphophosphoric Ether . . .	$P^2S^2(OC^2H^5)^2(SC^2H^5)^2$

2. *Metaphosphoric Sulphobromide*,  $PS^2Br$ .—This appears to be the substance insoluble in ether which is obtained in the preparation of the pyrosulphobromide. Michaelis attributes its production to the presence of phosphorus pentasulphide in the trisulphide used, and explains its formation by the following reaction:



With water this compound behaves like the pyrosulphobromide. With alcohol it forms a crystalline ether having the composition  $P^2S^2O^2(C^2H^5)^4$  (Michaelis).

3. *Orthophosphoric Sulphobromide*, or *Sulphophosphoryl Bromide*,  $PSBr^3$ .—This compound was discovered by Baudrimont, who obtained it by the action of hydrogen sulphide on phosphorus pentabromide (iv. 605). It is also produced, as above stated, by heating the pyrosulphobromide either alone or with phosphorus pentabromide. But the easiest way of preparing it is to add 8 pts. of bromine by drops to a solution of 1 pt. phosphorus and 1 pt. sulphur in carbon sulphide, keeping the liquid constantly cool. When the action is ended, the liquid is quickly distilled over as large a flame as possible, and the first portion of the distillate, which usually contains carbon sulphide, is collected apart. Part of the sulphobromide collects in the crystalline form in the neck of the retort; the rest passes over and remains dissolved in the liquid contents of the receiver. This liquid is repeatedly treated with fresh quantities of water, till the yellow oil, which at first collects at the bottom, has solidified to a yellow crystalline mass. The substance thus obtained is a hydrate of orthophosphoric sulphobromide,  $PSBr^3 \cdot H^2O$ . It has an aromatic tear-exciting odour, a specific gravity of 2.7937 at 18°, melts at 35°, and is resolved at the same time into water and the pure sulphobromide. It does not fume in the air, but gradually decomposes, with evolution of hydrobromic acid.

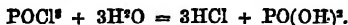
The anhydrous orthosulphobromide is obtained by treating the solution of the hydrate in carbon sulphide with calcium chloride, and remains, on evaporating the carbon sulphide, as a yellow liquid which for the most part does not solidify till touched with a solid body; it then forms a radio-crystalline mass. It melts at 38°, and exhibits in a high degree the phenomenon of superfusion. It dissolves easily in ether, carbon sulphide, phosphorus chloride, and phosphorus bromide, and crystallises from the last two solvents in yellow octohedrons belonging to the regular system.

Orthophosphoric sulphobromide is slowly decomposed by water in the cold, more quickly when heated, but a large portion passes over undecomposed with the aqueous vapour. The products of the decomposition are hydrobromic acid, large quantities of phosphorous acid and sulphur, and only small quantities of phosphoric acid and hydrogen sulphide, whereas the sulphochloride of phosphorus is resolved by water, as is well known, into hydrochloric acid, phosphoric acid, and hydrogen sulphide.

The formation of phosphorous acid and sulphur in the decomposition of the sulphobromide is explained by Michaelis as follows:—Sodium sulphophosphate,  $PS(NaO)^2$ , decomposed by free acids, yields hydrogen sulphide and phosphoric acid (Wüster). According to Michaelis, phosphorous acid and free sulphur are formed at the same time. Now, when  $PSCl^3$  and  $PSBr^3$  come in contact with water, either the chlorine (or bromine) or the sulphur may be removed by substitution. The former is the case with the sulphobromide, the products of its decomposition being  $HBr$  and  $PS(OH)^3$ , which latter is then resolved, partly by the further action of water, into  $P(OH)^3$ ,  $P(OH)^2$ , and  $SH^2$ ; whereas the sulphochloride exhibits the second form of decomposition, according to the equation:



the oxychloride then reacting with a further portion of water to form hydrochloric and phosphoric acids:



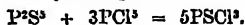
With *alcohol*, the sulphobromide forms ethyl monosulphophosphate,  $\text{PS}(\text{OC}^2\text{H}^5)^2$ .

Orthophosphoric sulphobromide does not volatilise wholly without decomposition, but is resolved by slow distillation into sulphur and the compound  $\text{P}^2\text{SBr}^4$  or  $\text{PSBr}^3 \cdot \text{PBr}^3$ :



The compound,  $\text{P}^2\text{SBr}^4$ , already mentioned as occurring amongst the products of the decomposition of the pyrosulphobromide by heat, is a yellow liquid which, when immersed in a mixture of ice and salt, solidifies to a white mass melting at  $-5^\circ$ . By repeated distillation it is entirely resolved into sulphur and  $\text{PBr}^3$ ; and by repeated washing with water it is converted into the hydrate of orthophosphoric sulphobromide,  $\text{PSBr}^3 \cdot \text{H}^2\text{O}$ .

**Sulphochloride.** *Sulphophosphoryl chloride*,  $\text{PSCl}^3$ .—This compound is easily prepared by heating phosphorus pentasulphide with the pentachloride at  $160^\circ$  in a sealed tube, in the proportions required by the equation:



It is a liquid boiling at  $126^\circ$  under a barometric pressure of 770 mm. Its vapour is extremely pungent, but when mixed with air it has a pleasant aromatic odour (T. E. Thorpe, *Chem. News*, xxiv. 136).

**Sulphochlorobromide**,  $\text{PS.Cl}^2\text{Br}$  (Michaelis, *Dent. Chem. Ges. Ber.* v. 146). To obtain this compound, ethylsulphophosphorous chloride,  $\text{PCl}^2(\text{SC}^2\text{H}^5)$ , (a colourless liquid boiling at  $172^\circ$ - $175^\circ$ ), is prepared by the action of phosphorous chloride on mercaptan, and bromine is added to it by drops in a vessel which is kept cool. The following reaction then takes place:



The resulting liquid is fractionally distilled; the portion boiling between  $160^\circ$  and  $180^\circ$  is agitated with water till no further action is perceptible; and the remaining liquid is separated from the water, dehydrated with calcium chloride, and freed by gentle heating from absorbed hydrochloric and hydrobromic acids.

Phosphorus sulphochlorobromide is a faintly yellow liquid having an aromatic pungent odour like that of the sulphochloride. It begins to boil at  $150^\circ$ , but the boiling point soon rises, the liquid undergoing partial decomposition, with separation of sulphur. It offers considerable resistance to the action of water, and, like the sulphochloride, may be partly distilled with water without decomposition. For complete decomposition it must be heated with water to  $150^\circ$  in a sealed tube for 4 hours. The products of decomposition are: free sulphur, hydrogen sulphide, phosphoric acid, and phosphorous acid, together with hydrochloric and hydrobromic acids. The quantity of free sulphur is exactly the half of that which is obtained by the decomposition of phosphorus sulphobromide.

#### PHOSPHORUS: OXIDES, OXYGEN-ACIDS, and OXYGEN-SALTS.

**Hypophosphorous Acid**,  $\text{H}^2\text{PO}^2$ . This acid is generally said to be an uncrystallisable syrup. J. Thomsen, however, has obtained it as a snow-white crystalline mass, melting at  $17.4^\circ$ . The dilute solution, obtained by decomposing the barium salt with sulphuric acid, is first boiled down rapidly in a porcelain dish, and the evaporation completed in a platinum dish without ebullition, the temperature being allowed to rise gradually to  $105^\circ$ , at which most of the water can be driven off. The liquid is then filtered hot, and the heating continued gradually up to  $130^\circ$ . After 10 minutes at this temperature the acid is transferred to a bottle, and cooled below  $0^\circ$ . It exhibits strongly the phenomenon of superfusion, but crystallises when touched with a glass rod, or more readily by the addition of a crystal of the same acid (*Dent. Chem. Ges. Ber.* vii. 994).

**Metallio Hypophosphites** (Rammelsberg, *Chem. Soc. J.* [2], xi. 1; *Dent. Chem. Ges. Ber.* v. 492).—The *sodium salt*,  $\text{H}^2\text{PO}^2 + \text{HFO}$ , forms small undeterminable deliquescent crystals which become anhydrous at  $100^\circ$ . The *thallium salt*,  $\text{H}^2\text{TlPO}^2$ , forms anhydrous crystals belonging to the rhombic system. The *ammonium salt*,  $\text{H}^2(\text{NH}^4)\text{PO}^2$ , the *barium salt*,  $\text{H}^2\text{BaP}^2\text{O}^4 + \text{H}^2\text{O}$ , and the *calcium salt*,  $\text{H}^2\text{CaP}^2\text{O}^4$ , also crystallise in the rhombic system. The *magnesium, zinc, nickel, and cobalt salts*, which contain 6 mols. water, form well-developed crystals belonging to the regular system.

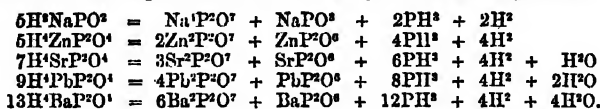
All the hypophosphites, excepting those of thallium, calcium, cadmium, and lead,

contain water of crystallisation, which they give up completely and without decomposition at temperatures between  $100^{\circ}$  and  $200^{\circ}$ ; the nickel and cobalt salts, however, cannot bear without decomposition a temperature higher than  $130^{\circ}$ – $140^{\circ}$ .

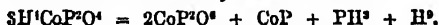
The decomposition of hypophosphites by heat does not in any case take place in the manner supposed by H. Rose (iv. 524), that is to say, into hydrogen phosphide, water, and a pyrophosphate, but in one of the two following ways:—

(1). The residue consists of a mixture of pyrophosphate and metaphosphate, and when dissolved in water leaves a small quantity of red phosphorus. The *alkali salts* (Na, Li, K), leave, on ignition, a residue consisting of 1 mol.  $R_2P_2O_7$  and 1 mol.  $RPO_3$  (R denoting a univalent metal), containing therefore, like the hypophosphite itself,  $\frac{1}{2}$  at. metal to 2 at. oxygen. No water is given off. The hypophosphites of *magnesium, zinc, and manganese* yield a residue containing 2 mols. pyrophosphate to 1 mol. metaphosphate; in those of *strontium, calcium, cerium, and cadmium*, this ratio = 3 : 1; in the *lead salt*, 4 : 1; and in the *barium salt*, 6 : 1.

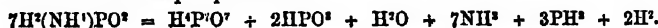
These modes of decomposition are represented by the following equations:



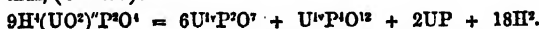
(2). The hypophosphites of *nickel and cobalt* leave, when ignited, a mixture of metaphosphate and phosphide, the latter of which gives the residue a black colour, and renders it almost insoluble in hydrochloric acid:



(3). *Ammonium hypophosphite* and *Uranyl hypophosphite* differ from all the other salts in their mode of decomposition by heat. The *ammonium salt* gives off ammonia, phosphine, hydrogen, and water, and leaves a residue consisting of 1 mol. pyrophosphoric and 2 mols. metaphosphoric acid:



The *uranyl salt*, which is yellow and sparingly soluble, decomposes with inflammation and explosive violence, giving off hydrogen and leaving a mixture of 3 mols. uranous pyrophosphate, 1 mol. uranous metaphosphate, and 1 mol. uranous monophosphide; thus, (U = 240):



The ratio of the number of atoms of phosphorus in the residue to the number which escape as gas in the decomposition of the several salts is as follows:

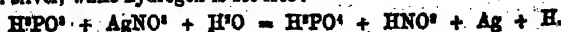
5 : 1	in the case of	Ni and Co
3 : 2	"	Na, Li, Mg, Zn, Mn.
4 : 3	"	Sr, Ca, Ce, Cd
5 : 4	"	Li, Pb
7 : 6	"	Ba,

but never 1 : 1, as formerly supposed.

The hydrogen of the hypophosphites behaves as follows. The sodium, potassium, thallium, magnesium, zinc, and manganese salts give off no water, the hydrogen being given off  $\frac{1}{2}$  free,  $\frac{1}{2}$  combined with phosphorus. All the other salts give off, together with hydrogen and phosphine, small quantities of water, the hydrogen of which amounts to  $\frac{1}{2}$ ,  $\frac{1}{3}$ , or  $\frac{1}{4}$  of the entire quantity of gas. Whether the evolved gas is spontaneously inflammable or not, depends altogether on accidental circumstances.

*Reducing Power of Hypophosphorous and Phosphorous Acids.*—The following experiments on the reducing power of these acids and their salts have been made by Rammelsberg (*Chem. Soc. J.* [2], xi. 13).

*Phosphorous Acid and Silver Salts.*—With excess of silver nitrate, 1 mol.  $H^{\cdot}PO^{\cdot}$  reduces 1 at. silver, while hydrogen is set free:

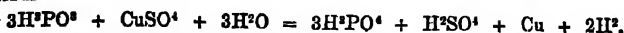


*Barium hypophosphite and Silver Salts.*—1 mol.  $H^{\cdot}Ba^{\cdot}PO^{\cdot}$ , with an excess of silver nitrate, gave 5Ag, and with silver sulphate, 5.5 Ag. Admitting 6Ag, we should have  $H^{\cdot}Ba^{\cdot}PO^{\cdot} + 6AgNO^{\cdot} + 4H^{\cdot}O = 2H^{\cdot}PO^{\cdot} + 4HNO^{\cdot} + Ba^{\cdot}NO^{\cdot} + 6Ag + 2H^{\cdot}$ .

The reducing power of the molecules  $H^{\cdot}PO^{\cdot}$  and  $H^{\cdot}P^{\cdot}O^{\cdot}$  seems to be as 1 : 3.

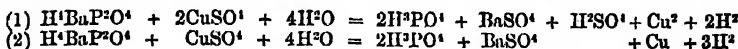
*Phosphorous Acid and Copper Salts.*—An excess of  $H^{\cdot}PO^{\cdot}$  decolorises the solution, cuprous oxide being formed. When the cupric sulphate is in excess, metallic copper

is separated, after boiling for some time, and 1 at. copper is reduced for every 3 at. phosphorus:



*Barium phosphite* is not changed by boiling with a solution of copper; when free sulphuric acid is added, a very small quantity of the metal is precipitated.

*Hypophosphorous Acid and Copper Salts.*—Hypophosphorous acid, heated with solution of cupric sulphate to  $55^{\circ}$ – $60^{\circ}$ , forms a precipitate of cuprous hydride,  $\text{Cu}^2\text{H}^2$  (Würtz, iv. 524). H. Rose (*Pogg. Ann.* lviii. 212) asserted that the reduction of copper by this acid was not attended with evolution of hydrogen. Rammelsberg finds that when barium hypophosphite is heated with excess of cupric sulphate, the precipitation of metallic copper takes place only at the boiling point of the liquid, and in the proportion 2 at. copper to 1 at. barium: consequently hydrogen must be evolved; further, that when free sulphuric acid is added, reduction begins below  $100^{\circ}$ , and the quantity of metal reduced is only half of what it was in the preceding case. The reactions in the two cases are:



The hydrogen is evolved with great rapidity.

*Sodium hypophosphite* with an excess of copper salt gives, Na : Cu = 1 : 1 at.; but the reaction requires continued boiling.

**Phosphoric Acid.** On the compound of phosphoric anhydride with boric anhydride,  $\text{P}^2\text{O}^5 \cdot \text{B}^2\text{O}^3$ , and on the reaction of phosphoric anhydride with boric chloride, see p. 207.

*Estimation of Phosphoric Acid.*—The two following methods are given by C. E. Munroe (*Sill. Am. J.* [3], i. 329).—1. To the boiling phosphate solution a weighed quantity of pure aluminium sulphate, previously dissolved, is added. A solution of mercuric chloride is then added, and finally pure sodium hydrate, until a precipitate of mercuric oxide is obtained which remains undissolved. To hasten the operation the precipitate is allowed to settle, and the supernatant liquid poured upon the filter. The gelatinous precipitate is then evaporated to complete dryness, filtered by the aid of a filter-pump, ignited, and weighed. The increase of weight over that of the alumina used is phosphoric oxide. The filter burns very slowly. Test analyses performed upon anhydrous disodic phosphate and crystallised ammonio-sodic phosphate gave very satisfactory results. The method appears, however, to be applicable with advantage only to the alkaline phosphates.

2. The second method is a modification of Rose's well-known mercury process. A boiling solution of the phosphate in nitric acid is precipitated with mercurous nitrate, a small quantity of mercuric nitrate is added, and then pure caustic soda, till a permanent red precipitate is obtained. The filtrate tested with molybdic acid does not exhibit a trace of phosphoric acid. The precipitate, consisting of mercurous phosphate and a little free mercuric oxide, is carefully separated from the filter, and intimately mixed in a porcelain crucible with a weighed quantity of cupric oxide; the filter is then laid upon the oxide and the whole ignited. The increase in weight of the crucible and cupric oxide gives the amount of phosphoric anhydride. By this method phosphoric acid may be separated from all bases except ferric and uranic oxides. From alumina the separation is perfect.

According to J. König (*Zeitschr. anal. Chem.* 1871, 473) the precipitation of phosphoric acid by *molybdic acid* is more or less prevented by ammonia salts when present in large quantity, the salts which act most injuriously in this respect being the oxalate and citrate. E. Richters (*ibid.* 469) also observes that certain salts, as well as free hydrochloric acid, interfere with the precipitation, but that ammonium nitrate promotes it in a very great degree; he therefore recommends a solution of this salt for washing the precipitated phosphomolybdate.

J. Parry (*Chem. News*, xxv. 279) recommends the use of an aqueous solution of ammonium molybdate, since in a strongly acid solution the precipitation is very slow.

Fresenius, Neubauer & Luck (*Zeitschr. anal. Chem.* x. 133) have examined the methods generally used for the estimation of phosphoric acid, with especial reference to the valuation of phosphatic manures.

1. Of the gravimetric methods, they find that the molybdenum method is the most accurate, provided it be performed in the following manner: The solution of 0.5 gram of the substance, in about 8 c.c. strong hydrochloric acid, is evaporated to dryness; the residue, after moistening with 2 c.c. hydrochloric acid, is dissolved in 10 c.c. nitric acid (sp. gr. 1.2); the solution diluted with water, filtered, and again evaporated; the

residue redissolved in 5 c.c. nitric acid; and the liquid digested for 12 hours at 40° with 150–200 c.c. of a solution of ammonium molybdate in nitric acid containing 5 pts. molybdic trioxide. When a sample of the supernatant liquid no longer gives any turbidity with the molybdic acid solution, the precipitate is collected on a filter, washed with 100 pts. of the molybdic acid solution, 20 pts. nitric acid, and 80 pts. water, then dissolved in the smallest possible quantity of aqueous ammonia; the solution, approximately neutralised with hydrochloric acid, is precipitated with a mixture of magnesium sulphate, ammonium chloride, and ammonia; and the precipitated ammonium-magnesium phosphate is washed with ammonia-water, dried, and ignited in the usual way.

The bismuth, uranium, lead, mercury, and tin methods, are admissible only when iron and aluminium are absent; in the presence of either of these bodies, the methods in question cannot be used without considerable modifications, which rob them of all their special advantages. The use of tartaric or citric acid, to keep iron and aluminium in solution during the precipitation of phosphoric acid by magnesia, does not yield very satisfactory results, since basic magnesium tartrate or citrate is often precipitated with the phosphate, and because the solubility of the ammonio-magnesium phosphate is increased by the presence of ammonium tartrate or citrate.

The volumetric uranium method, as ordinarily used, is trustworthy only when alkalis and magnesia are the only bases present. If citric acid is used to keep iron and aluminium in solution during the titration, some uncertainty is introduced, as free citric acid increases the solubility of uranium phosphate, and thus tends to give low results, while ammonium citrate, by diminishing the delicacy of the ferrocyanide-test, tends to give high results. If lime is present, the results are apt to be low, since calcium phosphate partially separates from an acetic acid solution on heating, and thus a portion escapes the action of the uranium. This error may, however, be got rid of by reversing the process, and adding a cold acetic solution of the phosphate to a hot solution of uranium, till the ferrocyanide-test just ceases to act.

According to W. Jani (*Chem. Centr.* 1871, 230) the accuracy of the volumetric uranium method is not affected by the presence of ammonium salts, but an excess of acetic acid or an acetate seriously affects the result. It is best, therefore, to neutralise the free acid present, not by means of sodium acetate, but by carefully adding ammonia or soda till the solution is slightly alkaline, and then a few drops of acetic acid. With this precaution the results obtained by titration with uranium solution agree with those of the best gravimetric methods.

C. Schumann (*Zeitschr. anal. Chem.* 1872, 382) uses a solution of *uranic nitrate* for the titration in preference to the acetate, because the appearance of the reaction with potassium ferrocyanide is then more sharply marked and the solution may be kept without alteration, especially if acidulated with a few cubic centimeters of nitric acid, whereas the acetate is very apt to deposit a basic salt. To avoid, however, the presence of free nitric acid, when a large quantity of uranium solution has to be added, as in the analysis of phosphates very rich in phosphoric acid, Schumann mixes the phosphatic solution with a sufficient quantity of sodium acetate, this quantity bearing the same proportion to the entire liquid as in the titration (according to Schumann, 20 c.c. sodium acetate to 50 c.c. of the phosphoric acid solution). The error arising in the analysis of calcareous phosphates from the precipitation of calcium phosphate by long boiling is avoided in the method of Fresenius, Neubauer & Luck, by reversing the process and titrating the uranium solution warmed in the water-bath with the phosphoric acid solution (see above). Schumann avoids it by the employment of the so-called *pre-titration*—that is to say, by first determining the quantity of uranium solution required for about 10 c.c. of the phosphoric solution. This renders it possible, in the subsequent titration of a larger volume of the same liquid, to add at once the exact quantity of the uranium solution required, within a few cubic centimeters, so that prolonged boiling may be dispensed with. The titration is conveniently performed in a flask which is heated, with frequent agitation, over a free flame, and the addition of the uranium solution is discontinued as soon as two drops of the liquid spread upon a porcelain plate, with a drop of ferrocyanide solution let fall as nearly as possible in the middle, form a distinct ring of uranium ferrocyanide which does not disappear on renewed boiling.

Among gravimetric methods, Schumann finds that the determination as *ammonio-magnesium phosphate* gives perfectly trustworthy results, provided the following directions are observed. The ammonio-magnesium phosphate must be kept, both during precipitation and during washing, in an ammoniacal liquid containing at least 2.5 grms. of ammonia in 100 cubic centimeters. In an ammoniacal liquid of this strength the ammonio-magnesium phosphate is quite insoluble, so that the correction of 0.001 grm. of magnesium pyrophosphate for every 54 c.c. of liquid, formerly recommended by Fresenius, may be dispensed with.



The exactness of the composition of the precipitated ammonio-magnesium phosphate was demonstrated by taking two equal quantities of a solution of disodic phosphate, evaporating one to dryness, igniting, and weighing the residue of sodium pyrophosphate; then precipitating the other as ammonio-magnesium phosphate, igniting the precipitate, and weighing the resulting magnesium pyrophosphate. The quantities of phosphoric acid calculated from these two determinations were almost exactly the same, viz. 0.1171 gram from the first and 0.1167 from the second. A second precipitation of the ammonio-magnesium phosphate is therefore superfluous, and indeed injurious, inasmuch as the dissolved precipitate is not completely reprecipitated by ammonia alone.

The excess which sometimes occurs in the estimation of phosphoric acid as magnesium pyrophosphate, in consequence of the simultaneous precipitation of basic magnesium salts, may be avoided by using only a slight excess of magnesia mixture, the solution being brought down to a determinate volume, and the quantity of magnesia mixture required for each precipitation approximately calculated. The liquid should be made ammoniacal before the addition of the magnesia mixture, unless the ammonia used is very dilute, and the precipitate must be washed with aqueous ammonia of 2.5 p.c. till a few drops of the wash-water do not exhibit the slightest turbidity on addition of silver nitrate. In case the liquid has acquired a high temperature, in consequence of chemical action taking place within it—as, for example, when a molybdenum precipitate is dissolved in strong ammonia, and the ammonia neutralised with hydrochloric acid—it must be left to cool before precipitation. There is no occasion to boil the magnesia precipitate for more than 12 hours, unless the quantity of phosphoric acid present is extremely small.

According to L. Brunner (*Zeitschr. anal. Chem.* 1872, 30), a solution of magnesium sulphate mixed with a certain quantity of sal-ammoniac gives with ammonia a precipitate of magnesium hydrate, when the temperature of the solution exceeds 60°. This circumstance must be taken into account in the analysis of artificial manures, when the phosphoric acid has to be determined in the filtrate from a precipitate of calcium oxalate which has been washed with boiling water.

E. W. Parnell (*Chem. News*, xxiii. 145) points out the insolubility of ammonio-magnesium phosphate in an ammoniacal liquid containing excess of magnesia. He recommends that the precipitation be performed in a hot dilute ammoniacal solution, in which case no magnesia will be carried down with the precipitate.

To determine phosphoric acid in presence of aluminium and iron (which preclude the immediate use of the uranium method), G. Villo (*Compt. rend.* lxxv. 344) mixes the hydrochloric acid solution with citric acid and excess of ammonia, and precipitates with excess of *magnesium chloride*, dissolves the precipitate in a small quantity of nitric acid, and estimates the phosphoric acid volumetrically with uranic acetate. According to his observations, the excess of magnesium chloride used for the precipitation counteracts the solvent action of the ammonium citrate, and more especially of the calcium citrate, on the ammonium-magnesium phosphate.

**Analysis of Phosphorite.**—When nitric acid acts on a phosphorite, the greater part of the iron remains undissolved, and with it a small portion of the phosphoric acid. Cold 5 p.c. sulphuric acid dissolves very little iron, and all but 0.1 p.c. of the phosphoric acid. Hydrochloric acid, however, takes up the whole of the phosphoric acid and iron; for the analysis therefore it is best to dissolve the phosphorite in hydrochloric acid.

For the determination of the phosphoric acid, Fresenius, Neubauer and Luck give the preference to the molybdenum method in all cases where scientific accuracy is desired; but for commercial purposes, the following method, which takes up much less time, and is sufficiently exact, may be advantageously employed.

110 c.c. of 5 p.c. sulphuric acid are taken; 5 grams of the very finely-ground phosphorite are placed in a mortar, rubbed slowly with some of the acid till brought to a soft paste, then diluted with water, and the suspended matter is decanted into a flask graduated for 253 c.c., the residue being treated as before. When both phosphorite and acid have been thus brought into the flask, the whole is agitated from time to time during four hours. The flask is next filled up to the mark, and then contains 250 c.c. of liquid (the solid matter occupying 3 c.c.); the solution is filtered; 100 c.c. of the filtrate are placed in a flask graduated for 200 c.c., treated with excess of caustic soda, and then with acetic acid, till it ceases to diminish the precipitate; the flask is then filled to the mark, and the solution after standing in the cold is filtered; the precipitate is weighed, and reckoned as ferric phosphate. The phosphoric acid in the solution is determined by the improved volumetric uranium method already mentioned (p. 988). The known quantity of uranium acetate employed is mixed with sodium acetate and acetic acid, and kept at a temperature of 30°–40° during the titration.

*Analysis of Superphosphates* (Fresenius, Neubauer & Luck, *loc. cit.*)—In lixiviating a superphosphate for the purpose of dissolving out the soluble phosphate, the material should not be very finely divided, as in that case the quantity of phosphoric acid will come out rather too high. The lixiviation is best performed by the method given by Fresenius in his *Anleitung zur quantitativen Analyse*. The phosphoric acid may then be determined by the molybdenum method or by the method last described.

Superphosphates often contain 'reduced phosphates'—that is to say, phosphates in which part of the soluble phosphoric acid has returned to the insoluble state, in consequence, according to some authorities, of the action of monocalcic phosphate on oxide of iron or alumina; according to others, from the action of the same body on undecomposed tricalcic phosphate. For the estimation of these reduced phosphates, sodium bicarbonate and ammonium oxalate have been recommended. To test the accuracy of the results obtained by their use, experiments were made on the precipitate obtained by adding excess of ordinary sodium phosphate to calcium chloride (chiefly dicalcic phosphate), which may be taken as a type of reduced phosphate. Prolonged boiling with sodium bicarbonate removes only about half the phosphoric acid present in this substance; half-an-hour's boiling with ammonium oxalate removes nearly all the phosphoric acid; but as ammonium oxalate also acts energetically upon natural phosphorite, the results obtained with it cannot be depended upon. A solution of neutral ammonium citrate, sp. gr. 1.00, was found, however, to answer the purpose required; it had practically no action on natural phosphorite, and decomposed the precipitated phosphate almost completely.

To estimate the reduced phosphate, two portions of the superphosphate, each weighing 2 grams, are lixiviated with water. In one of the residues thereby obtained, the unattacked and reduced phosphoric acid are determined together (*a*); the other is treated with ammonium citrate, as above described, to remove the reduced phosphoric acid; and in the residue thus obtained the amount of phosphoric acid (*b*) is determined after ignition with sodium carbonate, in the manner described for the analysis of phosphorite. This gives the amount of unattacked phosphoric acid, and the difference between *a* and *b* gives the quantity of reduced phosphoric acid in the superphosphate.

R. Warington (*Chem. Soc. J.* [2], ix. 584) finds that the exhaustion of superphosphates with hot water yields, according to circumstances, sometimes a larger, sometimes a smaller, proportion of soluble phosphates than exhaustion with cold water. If the superphosphate contains soluble aluminium salts, it will yield less soluble phosphate when boiled with water than when exhausted with cold water: this is shown by the fact that alum added to a cold solution of superphosphate produces no change, but on applying heat aluminium phosphate is precipitated. Ferric salts, on the other hand, give an immediate precipitate in the cold. Most superphosphates contain traces of soluble aluminium salts; those prepared from aluminous phosphates may contain a considerable quantity; the amount, however, depends much on the manner of manufacture. The solutions of such superphosphates in cold water become turbid on boiling.

It appears from the above that the soluble phosphate should always be extracted with cold water. The residue then yields a further trifling amount of phosphoric acid on boiling, arising probably from decomposition of reduced phosphates. The best method of extracting soluble phosphate is to take 10 grams of the superphosphate and elutriate them in a mortar with 1 litre of cold water. The water and suspended matter are poured into a bottle and shaken at frequent intervals during three hours. 100 c.c. of the solution correspond with 1 gram of the superphosphate.

The soluble phosphate is usually estimated by precipitation with ammonia, with or without calcium chloride, according to the proportion of lime in the solution. This method is liable to several errors; the results should be checked by some other method.

The soluble phosphate may be accurately estimated by uranium acetate if alumina be absent, or if alumina has been previously removed as phosphate by ammonium acetate.

A method available under all circumstances is to precipitate the solution of superphosphate with excess of ammonium oxalate, and treat the filtered liquor containing the alumina and phosphoric acid with citric acid, ammonia, and magnesia mixture, determining the phosphoric acid as magnesium pyrophosphate.

The insoluble phosphates in superphosphate are generally estimated much above the truth. It is best to determine the *total* phosphate by one operation, and then estimate the insoluble by deducting the soluble phosphate. The total phosphate may be determined by solution in hydrochloric acid, and precipitation from a cold dilute solution with a small excess of ammonia, just sufficient to turn turmeric red. If, however, the superphosphate contains iron or aluminium, the hydrochloric solution should be neutralised as far as possible without producing a precipitate, and then treated with

excess of ammonium oxalate, and subsequently with citric acid and magnesia mixture, as already described.

G. Ville (*Compt. rend.* lxxv. 334) describes a simple apparatus for filtering precipitates under pressure in the estimation of phosphoric acid on natural phosphates.

Birnbaum a. Chojnacki (*Zeitschr. anal. Chem.* 1870, 203) discuss the several methods in use for the estimation of phosphoric acid in phosphorites, and give the preference to a modification of Chancel's bismuth method (iv. 543).

P. Gräsert (*ibid.* 356) describes the process used for estimating phosphoric acid in the Lahn phosphorites, which consists essentially in the application of the volumetric uranium method.

Joulié (*Moniteur Scientifique* [3], ii. 213-232) publishes Researches on the Estimation of Phosphoric acid in all products relating to Agriculture and Physiology.

Comparative experiments on the different methods of estimating phosphoric acid and separating it from bases have also been published by R. Schweizer (*Zeitschr. anal. Chem.* 1870, 84), and by J. Janowsky (*ibid.* 1872, 152-167).

A modification of the method of Reynoso and of Reissig (iv. 644), depending on the use of stannic oxide, is described by W. C. Williams (*Chem. Soc. J.* [2], viii. 383).

**Metallo Phosphates.** *Preparation of Crystallised Phosphates.*—W. Skey (*Chem. News*, xxii. 61) has prepared several phosphates in the crystalline state by mixing solutions of the corresponding metallic salts with a soluble phosphate, in such proportion that the mixture shall retain an acid reaction. If the precipitate forms slowly, it may separate at once in the crystalline state; if it appears immediately, it is gelatinous, but becomes crystalline after a longer or shorter time. In this manner the following crystallised phosphates have been obtained, most of them resembling native minerals: zinc phosphate (hopcite),  $\text{Zn}^2\text{P}^2\text{O}^6 + 5\text{H}^2\text{O}$ , and cadmium phosphate, not known as a natural mineral; calcium phosphate,  $\text{Ca}^2\text{H}^2\text{P}^2\text{O}^6 + 3\text{H}^2\text{O}$ , rhombic, isomorphous with pharmacolite, having an acid reaction; chromic phosphate, with  $24\text{H}^2\text{O}$ , having the constitution of delvauxin and the colour of chrome-alum; silver phosphate, crystallised only from solution in acetic acid; barium phosphate and strontium phosphate. The phosphates of copper, nickel, cobalt and iron were not obtained in the crystalline state, but they form double salts with the phosphate of magnesium and ammonium. Zinc phosphate forms crystalline compounds with the phosphates of cobalt and nickel.

*Action of Sulphurous Acid on Phosphates* (Gerland, *J. pr. Chem.* [2], iv. 97).—Different phosphates are variously acted on by sulphurous acid in aqueous solution: some are simply dissolved, while others are completely decomposed, a sulphite being formed, and phosphoric acid going into solution. From some compounds sulphurous acid withdraws a part of the base, so that from a basic compound a neutral or acid salt is produced; upon others, viz., tricalcic phosphate, sulphurous acid acts in a way different from any of the foregoing.

1. *Tricalcium phosphate* is easily soluble in sulphurous acid. Concentrated solutions are decomposed at temperatures above  $18^\circ$ , forming mono- and dicalcium-phosphate and calcium sulphite. Both concentrated and dilute solutions are decomposed into dicalcium-hydrogen phosphate and calcium sulphite by alcohol, when placed, at ordinary temperatures, in a vacuum, or more quickly when boiled under diminished atmospheric pressure. But by quickly heating and boiling at the ordinary pressure, crystals are deposited consisting of tricalcium phosphato-sulphite,  $\text{Ca}^2\text{P}^2\text{O}^6\text{SO}^2 + 2\text{H}^2\text{O}$ .

The same substance is deposited as a white crystalline precipitate when sulphurous acid is passed into a watery solution in which tricalcium phosphate is suspended. After complete solution of the phosphate is effected, the liquid is quickly boiled, and the precipitate collected. It differs from the above-mentioned mixture of dicalcium phosphate and calcium sulphite by its great stability; it may be heated to  $110^\circ$  without decomposition, but at a somewhat higher temperature it is broken up, and gives off watery vapour, mixed with sulphurous and sulphuric acid vapour and sulphur. It possesses disinfectant properties in a marked degree; it is stable, has no smell, is tasteless, does not affect linen or woollen cloths, and is obtained in a very convenient form, as a heavy, white, dry powder. A small quantity mixed with decaying animal matter at once removes its bad odour. Although unchanged in pure air, it undergoes slow oxidation when placed in air containing decomposing animal matter. The corresponding compounds of the other metals have not been obtained.

2. *Dicalcium-hydrogen phosphate* dissolves easily in sulphurous acid, the phosphate being again obtainable from this solution, unchanged. All these solutions retain the gas which they have absorbed with great energy, but the basic do so more energetically than the neutral phosphates.

3. *Basic and neutral magnesium phosphate* and *magnesium-ammonium phosphate* are easily dissolved by water containing sulphurous acid, the first two without decomposition; the last, when in excess, gives neutral magnesium phosphate.

4. *Basic and neutral manganese phosphate* behave in a similar manner to the magnesium phosphates. In the cold the solutions yield crystals composed chiefly of the neutral phosphate; by boiling, the crystalline basic phosphate is precipitated.

5. *Copper phosphate* is only slightly dissolved by sulphurous acid solutions. At ordinary temperatures crystals of cuproso-cupric sulphite are deposited; by boiling, a copper phosphate, probably of the same composition as the original phosphate, is obtained.

6. *Uranium phosphate* is but slightly soluble in sulphurous acid, being deposited again unchanged.

7. *Trisodium phosphate* takes up sulphur dioxide very readily; and alcohol separates sodium phosphate from the solution. The crystals saturated with sulphur dioxide form a solution which, on standing, separates into two distinct layers, which on being shaken, unite to form a homogeneous liquid.

8. *Bismuthic, stannous, stannic, and metastannic phosphates* are in no way acted upon by sulphurous acid.

9. *Silver, lead, and barium phosphates* are acted upon by an aqueous solution of sulphurous acid in the same way as by other strong acids, sulphites and free phosphoric acid being formed.

*Aluminium Phosphates.*—*Amblygonite* and *Montebasite* (Descloizeaux, *Compt. rend.* lxxii. 306; lxxiii. 1247; lxxv. 114; lxxvi. 319. Pisani, *ibid.* lxxiii. 1470; lxxv. 79. Rammelsberg, *Deut. Chem. Ges. Ber.* v. 78. See also *Chem. Soc. J.* [2], ix. 892; x. 126, 468, 793; xi. 481, 1113). The lithio-aluminic fluo-phosphates found at Penig in Saxony, and at Hebron in the state of Maine (U.S.), have hitherto been regarded as identical, and designated as *amblygonite*. In 1871, however, a mineral of similar composition, but supposed to differ from *amblygonite* in the relative proportions of its constituent elements, and in its optical properties, was found in the stanniferous strata of Montebas (Creuse), and was named *montebasite*. Subsequently this mineral was analysed by Pisani, v. Kobell, and Rammelsberg, who concluded that it was identical in composition with the *amblygonite* of Saxony; that from Hebron had not then been analysed. More recently, however, Pisani has analysed the American mineral, and finds that it is a hydrated fluo-phosphate of aluminium and lithium not containing sodium, whereas the Saxon mineral is an anhydrous phosphate of aluminium, lithium, and sodium; and Descloizeaux has shown that the two minerals differ in their optical properties. Further, it is now known that both these minerals occur in the stanniferous strata of Montebas, though in very different quantities, the more abundant being identical with the sodio-lithio-aluminic fluo-phosphate of Penig, the less abundant with the lithio-aluminic fluo-phosphate of Hebron; and it is proposed by Descloizeaux and Pisani to designate the former by the old name of *amblygonite*, the latter by that of *montebasite*.

Both minerals are triclinic. *Amblygonite* occurs in laminar masses, opaque or more or less translucent, and having a dull white or faint violet colour. It cleaves imperfectly, but with about equal facility, in two directions inclined at an angle of about  $105^{\circ} 44'$ , the reflected images from the two cleavage-surfaces differing slightly in brightness; also in two other directions making respectively with the two former a very obtuse angle of nearly  $162^{\circ}$ . These four cleavages determine the faces of the primary parallelepiped  $p\ m\ t$ , or  $OP.\ \infty P.\ \infty P'$ , or 001 110  $\bar{1}10$ , having its right upper edge replaced by a truncation-face  $i'$ . The angles of these faces are—

$$mt = 151^{\circ} 4';\ pm = 105^{\circ} 44';\ pt = 95^{\circ} 20';$$

$$i'm = 96^{\circ} 15';\ i't = 95^{\circ} 20';$$

$$pi' = 152^{\circ} 57' \text{ (calc.)},\ 152^{\circ} 10' \text{ (obs.)}$$

*Montebasite* occurs at Montebas, in small quantity, in greenish-white laminar masses, much more transparent than *amblygonite*; at Hebron also in laminar masses and in distinct four-sided prisms. Sp. gr. of the Montebas mineral = 3.010; of that from Hebron, 3.029. It exhibits the three principal cleavages  $p, m, t$ , the angles between which are—

$$mt = 135^{\circ} \text{ to } 136^{\circ};\ pm = 105^{\circ};\ pt = 89^{\circ} \text{ to } 89^{\circ} 11'.$$

The angle  $pm$  is nearly the same in both minerals; but the other angles differ widely in the two.

In *amblygonite* the optic axes are situated in a place which divides into two very unequal parts the acute angle  $pm = 74^{\circ} 16'$ . In the *montebasite* of Hebron, on the other hand, the plane of the optic axes is situated in the obtuse angle  $pm$ , and traverses the edge  $t$ , but is not quite normal to  $m$ , since it gives angles of  $82^{\circ}$  with  $m$ .

and 23° with *p*. The character of the coloured rings shows that in montbrasite, both from Montebbras and from Hebron, there coexists with the horizontal a well-marked inclined dispersion, and these are peculiar to the crystals of the triclinic system. In amblygonite from Montebbras the appearance of the bars traversing the central ring of each system indicates very distinctly a *twisted* dispersion, which is also characteristic of the triclinic system.

Amblygonite melts easily in the flame of a spirit-lamp, without decrepitation, but with slight tumefaction, to a white opaline glass. To the blow-pipe flame it imparts a reddish yellow colour, due to the occurrence of sodium and lithium in about equal proportions. The optical properties of the amblygonite of Montebbras agree exactly with those of the Saxon mineral.

Montebbrasite melts before the blowpipe to a white enamel, and colours the flame a fine red, without any yellow tinge. In the spectroscopic it exhibits the lithium line. Heated in a tube it decrepitates more or less strongly (especially that of Montebbras), giving off water which has an acid reaction and corrodes the glass strongly (Pisani).

The difference of chemical composition of amblygonite and montebbrasite is shown by the following analyses :—

	Amblygonite						Montebbrasite	
	From Montebbras			From Penig			From Montebbras	From Hebron
	Pisani	v. Kobell	Rammelsberg	Rammelsberg	Rammelsberg	Pisani		
Fluorine . . . . .	8.20	10.40	9.00	10.06	8.11	9.44	3.80	5.22
Phosphoric anhydride	46.15	46.85	45.91	48.55	47.58	48.00	47.15	46.65
Alumina . . . . .	33.82	37.60	35.50	36.36	36.88	36.26	36.90	36.00
Lithia . . . . .	8.10	9.60	6.70	7.06	6.68	6.68	9.84	9.75
Soda . . . . .	2.28	0.59	5.30	0.93	3.29	3.29	—	—
Potash . . . . .	—	—	—	0.40	0.43	0.43	—	—
Lime . . . . .	—	—	0.50	—	—	—	—	—
Manganese oxide . .	0.40	—	—	—	—	—	—	—
Silica . . . . .	—	—	0.60	—	—	—	—	—
Water . . . . .	1.10	0.14	0.70	—	—	—	4.75	4.20
	100.05	105.18	104.21	104.26	102.97	104.10	102.44	101.82

Von Kobell (*Jahrbuch f. Mineralogie*, 1873, 317) considering that there is some confusion in the use of the name montebbrasite applied by Descloizeaux to the hydrated lithio-aluminic fluo-phosphate occurring at Montebbras and at Hebron, proposes to discard this name altogether and designate the mineral in question as Hebronite. He has examined more particularly a specimen of hebronite from Auburn in Maine. This variety colours the blowpipe strongly reddish-yellow, the red colour of the lithium being altered by the small quantity of sodium contained in the mineral. The hebronite of Auburn, and also that of Paris in Maine, exhibit a rather strong greyish phosphorescence when heated. The specific gravity of the Auburn hebronite is 3.06. Its analysis gave—

P <sup>2</sup> O <sup>5</sup>	Al <sup>2</sup> O <sup>3</sup>	Li	Na	F	H <sup>2</sup> O
40.00	37.00	3.44	0.79	5.50	4.50 = 100.23

agreeing with the formula :  $3(\text{Al}^2\text{O}^3.\text{P}^2\text{O}^5) + \text{Li}^2\text{F}^2 + 2\text{H}^2\text{O}$ .

*Calcium Phosphates*.—1. *Native*, from Canada, occurring in a bed about five meters thick, partly in crude masses (A), partly in prismatic crystals (B), has been analysed by R. Hutton (*Chem. News*, xxi. 150). Both varieties are partly green and bluish-green, partly red.

Ca <sup>2</sup> P <sup>2</sup> O <sup>5</sup>	CaF <sup>2</sup>	CuCl <sup>2</sup>	CaCO <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	H <sup>2</sup> O	Sand	Sp. g.
A. 88.61	7.22	0.06	4.47	—	0.08	0.10 = 98.54.	3.142
B. 90.82	5.70	0.14	0.38	0.40	0.32	0.10 = 97.80.	3.166

On the wide diffusion of apatite as a constituent of eruptive rocks and basalts, see F. Zirkell (*Jahrbuch f. Mineralogie*, 358, 801; *Jahresh. f. Chem.* 1870, 1343, 1362).  
*Francolite*.—This name is given by Maskelyne a. Flight (*Chem. News*, xxii. 280) to a mineral from Cornwall allied to staffelite (1st Suppl. 1037), occurring in aggregates

and intersecting twins of the hexagonal form  $\infty P \cdot mP$ , wherein  $mP$  denotes a very obtuse pyramid. Analysis gave numbers agreeing approximately with the formula:  $5Ca^{2+}P^{5+}_2O^{10-}_4 \cdot CaCO_3 \cdot CaF_2$

$Ca^{2+}P^{5+}_2O^{10-}_4$	$CaF_2$	$CaCO_3$	$Fe^{2+}O^{2-} \cdot Mn^{2+}O^{2-}$	$Na_2O$	$H_2O$
83.261	7.683	5.104	0.913	0.694	1.593 = 99.248

On the question whether staffelite is a distinct mineral species, see *Jahresb. f. Chem.* 1870, 1317.

For analysis of phosphatic concretions containing calcium phosphates from various localities, see *Jahresb. f. Chem.* 1870, 1316; 1871, 1219.

On the occurrence and formation of the phosphorite found on the Dniester in Russian Podolia, Galicia and Buckowina, see Schwachhöfer (*Wien. Akad. Ber.* lxiii, [2], 809; *Chem. Soc. J.* [2], x. 56). On the great phosphoritic zone of Russia, see Grewingk (*Jahrbuch. f. Mineralogie*, 1871, 757; *Chem. Soc. J.* [2], x. 58).

**Bone Phosphates.**—To determine the constitution of the calcium phosphate of bones, C. Aebv (*J. pr. Chem.* [2], v. 308; vi. 169) has analysed bones calcined by a natural process, as they occur in caves and in the form of fossil ivory in diluvial deposits. According to his analysis, such bones consist of 1 mol. orthophosphate,  $3CaO \cdot P^{5+}_2O^{10-}_4$ ,  $\frac{1}{2}$  mol. water of crystallisation,  $\frac{1}{2}$  mol. basic water,  $\frac{1}{2}$  mol. lime in excess, and  $\frac{1}{2}$  mol. carbon dioxide as an essential constituent. The carbon dioxide which exists in this form may be driven off, together with water of crystallisation, by heating to  $450^\circ$ , and cannot be restored by treatment with ammonium carbonate. After ignition and addition of ammonium carbonate, the weight and composition of the bone phosphates are the same as after six hours' heating to  $450^\circ$ .

**Calcium Phosphates formed by Precipitation.**—E. Reichardt (*Zeitschr. anal. Chem.* 1873, 275) finds that when a dilute solution of calcium chloride is precipitated by a small quantity of sodium phosphate, a precipitate which dissolves on agitation is produced, the redissolution being apparently due to the presence of carbonic acid in the water. A further addition of sodium phosphate reproduces the precipitate, and it may be again dissolved by passing a current of carbonic acid through the mixture. After some repetitions of this operation, the liquid deposits shining crystals, which were found to be identical with Boedeker's tetra-hydrated dicalcic orthophosphate,  $Ca_2H^{2+}P^{5+}_2O^{10-}_4 \cdot 4H_2O$ .

When this compound is boiled with water, it is partially decomposed; the portion remaining undissolved gave results agreeing with the formula,  $Ca^{2+}P^{5+}_2O^{10-}_4 \cdot Ca_2H^{2+}P^{5+}_2O^{10-}_4 \cdot 3H_2O$ , and the solution yielded, on evaporation, a residue which, after ignition, gave numbers corresponding with the formula  $4CaO \cdot 3P^{5+}_2O^{10-}_4$ . This substance dissolves in 3325.5 pts. of water. See also W. C. Davis (*Chem. Soc. J.* [2], v. 673).

**Solubility in Carbonic Acid Water.**—C. P. Williams (*Chem. News*, xxiv. 306) has determined the solubility of various calcium phosphates used in agriculture. The pulverised material was diffused through a very large quantity of water, carbon dioxide was passed through the liquid for five or six hours at a temperature  $60^\circ$  to  $70^\circ$  F., and the quantity of phosphoric acid in the filtrate was determined in the ordinary way after supersaturation with nitric acid.

	$3CaO \cdot P^{5+}_2O^{10-}_4$ per cent.	1 pt. $3CaO \cdot P^{5+}_2O^{10-}_4$ re- quires of Carbonic Acid Water
Apatite from Canada . . . . .	89.27	222,222
The same, very finely powdered . . . . .	"	140,840
Bone-ash . . . . .	56.78	5,678
Burnt bones . . . . .	92.88	8,029
Adulterated bone-ash of commerce . . . . .	35.06	4,122*
South Carolina phosphate . . . . .	57.89	6,983
The same, finely powdered . . . . .	"	6,564
Guano phosphate from Orchilla . . . . .	49.87	8,008

R. Warrington (*Chem. Soc. J.* [2], ix. 80) has made experiments on the solubility of bone-ash when repeatedly treated with carbonic acid water. The materials used were a commercial bone-ash containing 33.68 p.c.  $P^{5+}_2O^{10-}_4$ , and a pure bone-ash containing 39.55 p.c. The ash was drenched with water, and carbon dioxide was passed into the water for 16 to 24 hours on three or more successive days, the ash being stirred from time to time. The water was then poured off and analysed, and the residue left each time was treated in the same manner for the preparation of the following solution.

\* This bone-ash probably contained  $CaO \cdot 2H^{2+}P^{5+}_2O^{10-}_4$ .

I. Experiments on the Solubility of Commercial Bone-ash.

Number of solution	Found in 10,000 parts of each solution															Total dissolved for 100 originally present in the Bone-ash
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	
P <sub>2</sub> O <sub>5</sub>	2.353	1.473	1.159	1.073	1.000	.970	1.288	1.173	1.110	1.026	.909	Not	.779	.631	.758	11.35
CaO	1.918	3.226	1.747	1.547	1.419	1.279	1.789	1.572	1.433	1.329	1.163	ana-	1.008	—	.951	11.34
MgO	1.695	.672	.221	.118	.070	.076	.191	.073	.066	.070	.053	lysed	.040	—	—	66.79

II. Experiments on the Solubility of Pure Ox Bone-ash.

Number of solution	Found in 10,000 parts of each solution								Total dissolved for 100 originally present in the Bone-ash
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	
P <sub>2</sub> O <sub>5</sub>	1.010	.634	.538	.581	.669	.662	.674	.696	4.19
CaO	1.376	1.188	.943	.919	.956	.892	.874	—	4.63
MgO	2.382	.526	.125	.063	.056	.045	.031	—	96.34

The whole effect produced by the carbonic acid water upon the pure bone-ash appears to have consisted in the removal of but a small quantity of the phosphoric acid and lime (the latter in somewhat larger proportion than the former), while nearly the whole of the magnesia was taken up. The magnesium salts in bone-ash appear, indeed, to be much more soluble than the calcium salts. Taking the mean of the last four experiments in the second table as representing the permanent solubility of the phosphates of the pure bone-ash, we have a solubility of 0.675 P<sub>2</sub>O<sub>5</sub> in 10,000 pts. of carbonic acid water; and reckoning the phosphoric acid as tricalcic phosphate, the solubility of this phosphate in carbonic acid water is 1 pt. in 6788.

**Copper Phosphates.**—Rammelsberg (*Pogg. Ann.* lxxviii. 383) found that, on dropping 3 mols. cupric sulphate into a hot solution of 2 mols. ordinary sodium phosphate, a precipitate is formed having the composition 2[(CuO)<sup>2</sup>P<sub>2</sub>O<sub>5</sub>] + CuO.P<sub>2</sub>O<sub>5</sub> + 3H<sub>2</sub>O. According to J. Weinck (*Ann. Ch. Pharm.* clvi. 57), the precipitate thus formed contains soda. In the perfectly washed precipitate dried at 100°–110°, he found, as a mean, 38.32 p.c. P<sub>2</sub>O<sub>5</sub>, 40.45 CuO, 8.84 Na<sub>2</sub>O, and 6.75 H<sub>2</sub>O, giving approximately the proportion 4P<sub>2</sub>O<sub>5</sub> : 9CuO : 2Na<sub>2</sub>O.\* He regards this substance as a mixture of several compounds, and suggests that other phosphates obtained by precipitation with sodium phosphate may also contain soda.

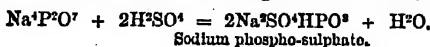
**Magnesium Phosphates.**—According to O. Popp (*Zeitschr. f. Chem.* 1870, 305), ammonium-magnesium phosphate, when heated, always exhibits the well-known appearance of ignition, provided it is free from foreign admixtures. The glow may, however, be weakened, or may not take place at all, if the phosphate contains calcium salts or other salts of magnesium, and especially if it contains a small quantity of silica. The glow takes place at a rather high temperature when all the water and ammonia have been already driven off, so that weighings before and after its appearance show no difference. This glow-phenomenon cannot be due to the conversion of the phosphoric into pyrophosphoric acid, since precipitated magnesium pyrophosphate, Mg<sup>2</sup>P<sub>2</sub>O<sub>7</sub> + 6H<sub>2</sub>O, likewise glows when raised to a strong red heat. Popp considers that it is caused by the passage of the substance from the crystalline to the amorphous state—in fact, by fusion; and that it must be regarded as analogous, though in the contrary direction, to that which takes place when vitreous amorphous bodies (amorphous arsenious oxide and fused boric oxide) assume, under certain conditions, the crystalline

\* The circumstance that this precipitate contains 11 mols. base to 4 mols. phosphoric acid, whereas the sodium phosphate contains only 8 mols. base to 4 mols. acid, explains the fact previously noticed by Rammelsberg, that the nitrate has an acid reaction. Weinck found, in contradiction to Rammelsberg, that this nitrate is precipitated by a small quantity of cupric sulphate (*Jahresb.* 1870, 385).

form. Arsenate of magnesium and ammonium does not glow when heated, apparently because the magnesia set free at the same time prevents the fusion of the arsenate. The incandescence which certain hydrated metallic oxides, as chromic oxide, ferric oxide, &c., exhibit when heated, admits also, according to Popp, of a similar interpretation, which at the same time serves to account for the great indifference of the resulting anhydrous oxides.

**Silver Phosphates.**—According to E. N. Horsford (*American Chemist*, i. 284) triargentic phosphate, heated to redness with pure sand, is converted into the corresponding metaphosphate.

**Sodium Phosphates.**—When sodium pyrophosphate is fused with 1 mol. of boric oxide, a phosphoborate of sodium is produced, which, by the action of water or alcohol, is decomposed into boric acid and ordinary sodium phosphate. If the pyrophosphate be heated with oil of vitriol till vapours of sulphuric acid are no longer evolved, and the product be then dissolved in water acidulated with phosphoric acid, the solution on evaporation yields brilliant plates of a salt having the constitution  $\text{Na}^+\text{SO}^+\text{HPO}^-\text{H}^+\text{O}$ :



An acid phosphate will give a similar result. The phospho-sulphate is permanent in air. It loses 1 mol. of water at  $200^\circ$ , and the second only at a red heat, when it is decomposed into sulphuric acid and pyrophosphate. Pure water resolves it into phosphoric acid and a sulphate.

On treating metaphosphoric acid with 2 mols. of sulphuric acid, a syrupy uncrystallisable liquid is produced, decomposed instantly by water into orthophosphoric and sulphuric acid. The solution is no longer precipitated by albumin. Hence we may conclude that a double acid corresponding with sodium phosphosulphate has been formed (Prévault, *Compt. rend.* lxxiv. 1249).

On the amount of Heat evolved in the Solution of Sodium Phosphate containing different Proportions of Water of Crystallisation, see Pfaunder (*Deut. Chem. Ges. Ber.* iv. 773; *Chem. Soc. J.* [2], ix. 1131).

**Thallium Phosphates.**—Observations on the isomorphism of these salts with the phosphates of the alkali-metals have been made by Rammelsberg (*Deut. Chem. Ges. Ber.* iii. 276). He thinks it probable that acid thallious phosphate, to which Lamy a. Descloizeaux (*Ann. Chim. Phys.* [4], xvii. 310) assigned the formula  $2\text{Tl}^+\text{HPO}^-\text{H}^+\text{O}$ , has really the composition  $\text{Tl}^+\text{HPO}^-\text{H}^+\text{O}$ , analogous to that of the sodium salt,  $\text{Na}^+\text{HPO}^-\text{H}^+\text{O}$ , with which it is isomorphous. *Monothallious orthophosphate*,  $\text{Tl}^+\text{H}^+\text{PO}^+$ , is, according to Rammelsberg, isomorphous with the ammonium salt,  $(\text{NH}^+)\text{H}^+\text{PO}^+$ . Lamy a. Descloizeaux describe a compound of thallious phosphate with ammonium phosphate containing  $(\text{NH}^+)\text{PO}^+$ ,  $(\text{NH}^+)\text{TiPO}^+$ , and isomorphous with the ammonium salt,  $(\text{NH}^+)\text{H}^+\text{PO}^+$ . The compound prepared by Rammelsberg according to the directions of Lamy a. Descloizeaux had, however, a different composition, and Rammelsberg therefore regards the salt in question as an isomorphous mixture of  $(\text{NH}^+)\text{H}^+\text{PO}^+$  and  $\text{Tl}^+\text{HPO}^+$ . He regards the hydrogen in phosphates as a so-called isomorphous constituent, and supposes that phosphoric acid itself is isomorphous with the phosphates  $\text{H}^+\text{R}^+\text{PO}^+$ ,  $\text{HR}^+\text{PO}^+$ ,  $\text{R}^+\text{PO}^+$ .

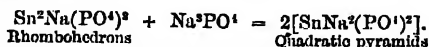
**Tin and Titanium Phosphates.**—Gustav Rose (*Berl. Akad. Monatsber.* Juli, 1867), by crystallising titanous acid from fused microcosmic salt, obtained flat plates which he regarded as anatase. W. Knop, however (*Ann. Ch. Pharm.* clvii. 363), found, by examination with polarised light, that they belonged to the rhombic, not to the quadratic system. They, moreover, had a specific gravity of only 2.0, whereas that of anatase is  $3.890^\circ\text{--}3.927^\circ$ . Further, on fusing them with potassium carbonate, dissolving in hydrochloric acid, and precipitating with ammonia, the filtrate was found to contain phosphoric acid, and quantitative analysis gave results from which Knop deduced the formula  $3\text{TiO}^+\text{P}^+\text{O}^+$ ; he therefore inferred that the crystals consisted of phosphotitanic acid. *Stannic acid* crystallised in like manner from microcosmic salt, yielded pyramidal crystals consisting of, according to Knop's analysis,  $2\text{SnO}^+\text{P}^+\text{O}^+$ , and two kinds of cubic crystals,  $\text{SnO}^+\text{P}^+\text{O}^+$  and  $3\text{SnO}^+\text{P}^+\text{O}^+$ , according to the proportions of the materials employed (*ibid.* elix. 36).

G. Wunder (*J. pr. Chem.* [2], iv. 330) finds, on the other hand, that all these compounds are double phosphates of tin or titanium and sodium.

Stannic oxide, fused with a mixture of borax and microcosmic salt, yields quadratic pyramids having the composition  $\text{SnNa}^+\text{P}^+\text{O}^+$ . Crystallised from microcosmic salt alone, it yields microscopic crystals which might be mistaken for cubes were it not for their action on polarised light; they have the composition  $\text{Sn}^+\text{Na}^+\text{P}^+\text{O}^+$ , and are sometimes accompanied by the quadratic prisms just mentioned. A goniometric examination of larger crystals of this species showed that they were not really cubes, but



rhombhedrons, the angles differing from a right angle by somewhat more than  $2^\circ$ . The formation of the quadratic prisms is facilitated when the stannic oxide is in relatively large quantity, or when borax is present. This is owing to the formation of trisodic phosphate, as was proved by direct experiment, the rhombhedrons being converted into the quadratic prisms, and *vice versa*, according as the flux contained less or more phosphoric acid :



Wunder attributes Knop's results to the fact of his having treated his crystals with fused phosphoric acid, whereby they were partly decomposed and the sodium removed.

The compound designated by Knop as phosphotitanic acid likewise contains sodium, and has a composition exactly analogous to that of the rhombhedronal tin salt, viz.:  $\text{Ti}^2\text{Na}(\text{PO}_4)^2$ . The crystals are rhombhedrons, differing but very slightly from cubes.

Attempts to prepare the compound  $\text{TiNa}^2(\text{PO}_4)^2$ , by adding basic sodium phosphate to the required flux, were unsuccessful (Wunder).

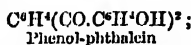
**PETHALEINS and PHTHALINS.** The name *phthalein* is applied by Baeyer (*Deut. Chem. Ges. Ber.*) to certain colouring matters produced by the combination of phthalic anhydride and phenols, monatomic or polyatomic, with elimination of one or more molecules of water. By the action of nascent hydrogen the phthaleins are converted into colourless compounds called phthalins, which, by oxidation in the air, are reconverted into phthaleins. Similar colouring matters are formed by the action of mellitic, pyromellitic, and oxalic acid on phenols in presence of sulphuric acid.

The phthaleins of resorcin, pyrogallol and naphthol have already been described : see FLUORSCHEIN (p. 524), GALLEIN (p. 534), NAPHTHOL (p. 830).

*Phenol-phthalein*,  $\text{C}^{20}\text{H}^{14}\text{O}^4$ .—When a mixture of 10 pts. phenol, 5 pts. phthalic anhydride, and 4 pts. strong sulphuric acid is heated to  $120^\circ$ – $130^\circ$  for several hours, a red mass is obtained which, when treated with boiling water, yields a resin, and this resin is converted by boiling with water into a yellowish powder, which dissolves in potash, yielding a fuchsine-coloured solution, from which hydrochloric acid precipitates the phenol-phthalein in white resinous flocks. The formation of this body is represented by the equation :



Phenol-phthalein is isomeric with phenyl phthalate :



and these two isomeric compounds appear to be formed simultaneously by the action of phenol on phthalyl chloride.

The solution of phenol-phthalein in potash is decolorised by zinc-powder, and on adding sulphuric acid to the solution phenol-phthalein,  $\text{C}^{20}\text{H}^{14}\text{O}^4$ , is precipitated in white granules. This compound forms with potash a colourless solution, which turns red on exposure to the air.

**PHTHALIC ACID**,  $\text{C}^8\text{H}^4\text{O}^4 = \text{C}^8\text{H}^4(\text{COOH})^2$ . This acid is formed by oxidation of naphthaquinone with nitric acid (Liebermann and Dittler, *Deut. Chem. Ges. Ber.* i. 945).

*Electrolysis.*—The aqueous solution of phthalic acid conducts the current slowly, no oxygen being evolved at the positive pole. Potassium phthalate is easily decomposed, hydrogen being evolved at the negative pole, and the solution becoming alkaline, while at the positive pole phthalic acid is separated, only a small portion of it being oxidised to carbon monoxide and dioxide, which escape with the oxygen (Bourdin, *Ann. Chem. Phys.* [4], xxii. 361).

*Bromophthalic acid*,  $\text{C}^8\text{H}^3\text{Br}(\text{COOH})^2$ , is formed by heating phthalic acid with bromine (in the proportion 4 : 5) and water to  $180^\circ$ – $200^\circ$ . A great part of the phthalic acid, however, remains unaltered, and may be separated by recrystallisation from water, the brominated acid remaining in the mother-liquor. The latter is converted into potassium salt, which is purified by repeated crystallisation from 90 p.c. alcohol, and the bromophthalic acid is separated by sulphuric acid and dissolved out by agitation with ether.

Pure bromophthalic acid is a white powder easily soluble in water, alcohol and ether. The *potassium salt*,  $\text{C}^8\text{H}^3\text{BrO}^4\text{K}^2 + 2\text{H}^2\text{O}$ , crystallises from hot alcohol in white shining deliquescent needles. The *barium salt*,  $\text{C}^8\text{H}^3\text{BrO}^4\text{Ba} + 2\text{H}^2\text{O}$ , is obtained from it by double decomposition. The *lead, copper, and silver salts*, obtained in like manner, are anhydrous. The *ethyl ether* is an oil having a faint yellow colour (A. Faust, *Ann. Ch. Pharm.* cl. 56).

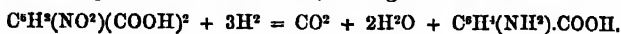
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3 B

**Dichlorophthalic acid**,  $C^6H^2Cl^2(COOH)^2$ , is obtained by boiling dichloronaphthalene tetrachloride,  $C^{10}H^6Cl^2.Cl^4$ , with ordinary nitric acid, and purified by repeated crystallisation from water. It dissolves easily in alcohol, ether, and hot water, and separates from the hot concentrated aqueous solution, sometimes not till after a day or two, in faintly yellowish prisms, often intergrown. It melts at  $183^{\circ}$ – $185^{\circ}$ , and by repeated sublimation is wholly converted into dichlorophthalic anhydride,  $C^6H^2Cl^2O^2$ , which melts at  $187^{\circ}$ , and resembles benzoic acid in appearance.

**Barium dichlorophthalate**,  $C^6H^2Cl^2O^4Ba$  +  $H^2O$ , separates on mixing an ammoniacal solution of the acid with barium chloride, in prisms which are sparingly soluble in water. The **calcium salt**,  $C^6H^2Cl^2O^4Ca$  +  $4H^2O$ , prepared in like manner, forms yellowish prisms, sparingly soluble in water (Faust).

**Nitrophthalic acid**,  $C^6H^3(NO^2)(COOH)^2$ , is obtained by digesting phthalic acid for 24 hours with a mixture of equal parts of red nitric acid and sulphuric acid, and precipitating with water. It crystallises from ether in pale yellow prisms, which melt at  $208^{\circ}$ – $210^{\circ}$ , being partly converted at the same time into the anhydride. It dissolves easily in water and in ether. By the action of tin and hydrochloric acid, it is converted into ordinary amidobenzoic acid, melting at  $173^{\circ}$ – $175^{\circ}$ :



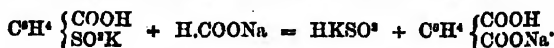
**Neutral potassium nitrophthalate**,  $C^6H^3(NO^2)O^4K^2 + H^2O$ , is precipitated from aqueous solution by alcohol in yellowish needles, permanent in the air, and easily soluble in water. From hot 90 p.c. alcohol it crystallises anhydrous. The **acid salt**,  $C^6H^4(NO^2)O^4K + H^2O$ , is precipitated on mixing a strong solution of the neutral salt with nitrophthalic acid, in white needles, less soluble in water than the neutral salt. The **ammonium salt**,  $C^6H^4(NO^2)O^4(NH^4)^2$ , is formed in large rhombic prisms on mixing a solution of the acid in strong ammonia with absolute alcohol, till a turbidity is produced. It dissolves easily in water, and crystallises therefrom with difficulty. The **acid ammonium salt**,  $C^6H^4(NO^2)O^4(NH^4)$ , separates on mixing the alcoholic solution of the neutral ammonium salt with nitrophthalic acid, in slender yellowish white needles, less soluble in water than the neutral salt. The **barium salt**,  $C^6H^3(NO^2)O^4Ba + xH^2O$ , crystallises from its supersaturated aqueous solution in shining yellowish laminae, containing a variable amount of crystallisation-water. It is but slightly soluble in water. The **zinc salt**,  $C^6H^4(NO^2)O^4Zn + \frac{3}{2}H^2O$ , prepared by boiling an aqueous solution of the acid with zinc oxide, is a yellow crystalline powder. The **lead salt**,  $C^6H^3(NO^2)O^4Pb + \frac{3}{2}H^2O$ , is a white slightly soluble precipitate. The **silver salt**,  $C^6H^3(NO^2)O^4Ag^2$ , is a white, sparingly soluble powder.

The **neutral ethylic ether**,  $C^6H^3(NO^2)O^4.(C^2H^5)^2$ , is easily formed by passing gaseous hydrogen chloride into the warm solution of nitrophthalic acid in absolute alcohol. It is a faintly yellow, scentless oil, which boils with rapid decomposition, at a temperature above  $300^{\circ}$  (Faust).

The **acid ethylic ether**,  $C^6H^4(NO^2)O^4.C^2H^5$ , is formed on passing gaseous hydrogen chloride into the cold alcoholic solution of the acid, and remains on evaporating the alcohol, as an oil which gradually crystallises. By boiling its aqueous solution with barium carbonate, a barium salt is obtained which crystallises from water in stellate groups of easily soluble prisms.

**Dinitrophthalic acid**,  $C^6H^4(NO^2)^2O^4$ .—An acid having this composition is obtained by the action of a mixture of nitric acid and sulphuric acid on nitranisic acid. It is very sparingly soluble in cold water, and crystallises from boiling water in colourless rhombic tablets. The **ammonium salt** dissolves easily in water, and crystallises therefrom in stellate groups of thin yellow needles. The **barium salt**,  $C^6H^4(NO^2)^2O^4Ba$ , is also nearly insoluble in boiling water (Engelhardt u. Latschinoff, *Zeitschr. f. Chem.* [2], vii. 262).

**Isophthalic Acid**. V. Moyer (*Ann. Ch. Pharm.* clvi. 265; clix. 1) prepares this acid by the action of sodium formate on potassium sulphobenzoate:



The isophthalic acid thus prepared dissolves easily in alcohol and ether, is nearly insoluble in cold water, sparingly soluble in boiling water, and separates therefrom on cooling in flocks which melt above  $300^{\circ}$ . The **methylic ether** melts at  $64^{\circ}$ – $65^{\circ}$ ; the **barium salt** contains 3 mols. water.

According to Storrs u. Fittig (*ibid.* cliii. 283) isophthalic acid (from xylene) dissolves in 460 pts. of boiling water, and in 7,800 pts. water at  $25^{\circ}$ . The **ethylic ether**  $C^6H^4(COOC^2H^5)^2$ , is a colourless liquid boiling at  $285^{\circ}$ , and solidifying at  $0^{\circ}$  to radio-crystalline mass.

**Nitro-isophthalic acid**,  $C^6H^3(NO^2)(COOH)^2$ , is prepared by boiling isophthalic

acid for three or four hours with fuming nitric acid, evaporating to dryness, and re-crystallising from water; or it may be purified by conversion into the calcium salt. It forms thin shining laminae which dissolve easily in water and in alcohol, and melt at  $248^{\circ}$ – $249^{\circ}$ . Together with this acid there is formed a small quantity of another acid melting at  $10^{\circ}$ – $15^{\circ}$  lower.

**Calcium nitro-isophthalate**,  $C^6H^3(NO_2)O^2Ca$  +  $3\frac{1}{2}H_2O$ , is sparingly soluble in cold water, and turns reddish on exposure to light. The **barium salt**,  $C^6H^3(NO_2)O^2Ba$  +  $2\frac{1}{2}H_2O$ , exhibits similar properties. The **ethyl ether** is unaffected by light, easily soluble in hot alcohol, sparingly soluble in cold alcohol, and in water. It melts at  $83.5^{\circ}$ .

**Amido-isophthalic acid**,  $C^6H^3(NH^2)(COOH)^2$ , crystallises from boiling water in laminae, from solutions containing acetic acid, and from alcohol, in prisms slightly soluble in cold water and in alcohol. It sublimes undecomposed when cautiously heated, but decomposes when rapidly heated. It forms very stable salts both with acids and with bases. The **hydrochloride**,  $C^6H^3(NH^2)O^2.HCl$  +  $H_2O$ , is easily soluble in water, nearly insoluble in strong hydrochloric acid. The **sulphate**,  $[C^6H^3(NH^2)O^2]^2.SO^2.H^2$  +  $H_2O$ , dissolves easily in water, and crystallises therefrom in concentrically-grouped prisms. **Cupric amido-isophthalate** is formed as a green precipitate of variable composition, when the hydrochloride of amido-isophthalic acid is mixed with cupric acetate (Storrs u. Fittig).

**Terephthalic Acid** may be formed from solid dibromobenzene by treating the latter in ethereal solution with sodium and methyl iodide, distilling off the methylic ether and the resulting hydrocarbon after the action is finished, and oxidising the latter, after it has been purified by fractional distillation, with potassium chromate and sulphuric acid (V. Meyer, *Deut. Chem. Ges. Ber.* iii, 753).

**PTHALIC CHLORIDE**,  $C^6H^2O^2Cl^2$ , is readily obtained by boiling gently for several days a mixture of 1 mol. phthalic acid and 2 mols. phosphorus pentachloride to which a little oxychloride is added. As soon as the evolution of hydrochloric acid ceases, the product is distilled from an oil-bath, and the chloride boiling at  $270^{\circ}$  is collected separately. It is a yellowish oily liquid, which is heavier than water, and decomposed by it but slowly. When exposed to moist air, it is gradually converted in beautiful monoclinic crystals of phthalic anhydride, boiling at  $275^{\circ}$  (Ador).

**PTHALYL**, or **DIPHTHALYL**,  $C^{10}H^4O^2 = (C^6H^4O^2)^2$ , (Ador, *Ann. Ch. Pharm.* cxiv, 229): Phthalic chloride is very readily acted upon by silver dust; by gradually adding 14 pts. of the latter to 10 pts. of the chloride, a solid mass is obtained, which, in order to finish the reaction, may be heated for some time in an oil-bath to  $150^{\circ}$ . The products consist of phthalic anhydride, a portion of which sublimes during the latter operation, a resinous body soluble in alcohol, and diphthalyl, which is isolated by exhausting the product repeatedly with boiling water and with alcohol. The dried residue is then heated in a combustion-tube, through which a slow current of dry carbon dioxide passes, the diphthalyl subliming as a light, orange-coloured crystalline mass, which may be purified by dissolving it several times in hot phenol, and reprecipitating it by alcohol. The pure compound has a pale yellow colour; it is insoluble in water, scarcely soluble in alcohol and ether, sparingly soluble in chloroform, carbon sulphide, and liquid hydrocarbons. Phenol and cold concentrated sulphuric acid are the only liquids which dissolve larger quantities of it. It melts a little above  $300^{\circ}$ , subliming at the same time in soft felted needles. The formation of diphthalyl is explained by the equation:



When diphthalyl is heated in a current of air, a sublimate is obtained, consisting of phthalic anhydride, a red resinous body, and unaltered diphthalyl.

**Diphthalylaldehydic Acid**,  $C^{10}H^4O^3$ , is produced by dissolving diphthalyl in hot caustic alkalis; on the addition of hydrochloric acid to the solution, a bulky precipitate of the new acid is obtained. After drying it is a white, bulky, indistinctly crystalline powder; it is insoluble in water, very sparingly soluble in alcohol, ether, chloroform, petroleum-naphtha, and benzene, but dissolves readily in hot phenol, cold caustic soda, and solutions of alkaline carbonates.

When rapidly heated it melts only above  $300^{\circ}$ , but on heating it for six hours to  $80^{\circ}$  it becomes perfectly liquid, and then consists of a mixture of phthalic acid, a little diphthalyl, and an acid which has the composition  $C^6H^4O^3$ , and melts between  $00^{\circ}$  and  $225^{\circ}$ .



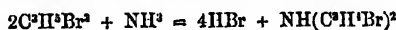
In order to obtain this monochloride, phthalic anhydride was heated with somewhat less than 1 mol. of phosphorus pentachloride. The product consisted of unaltered phthalic anhydride, phthalic dichloride, and the compound  $C^6H^4CPO^3$ , probably a combination of  $C^6H^4 \begin{Bmatrix} COCl \\ COCl \end{Bmatrix}$  with  $C^6H^4 \begin{Bmatrix} CO.OH \\ CO.Cl \end{Bmatrix}$ . It crystallises in long plates, melting at  $17^\circ$ . On heating it with silver-dust, it yields, besides phthalic anhydride and diphtalyl, a considerable quantity of diphtallic acid.

The resinous bye-products contain, besides diphtallic acid, several other compounds; of these, one having the composition  $C^{16}H^{10}O^1$  crystallises from boiling water in small white needles melting at  $240^\circ$ , with formation of phthalic anhydride. It is soluble in ammonia; silver nitrate produces in the neutral solution a white precipitate having the composition  $C^{16}H^{10}Ag^2O^3$ ; the corresponding barium salt is obtained by dissolving the acid in baryta water, and evaporating the solution in a vacuum. It crystallises in small plates having the composition  $C^{16}H^{10}BaO^3 + H^2O$ . When the ammonium salt is boiled with silver nitrate, reduction takes place, and a compound having the properties of diphtallic acid is formed. The compound  $C^{16}H^{10}O^1$  is therefore an anhydride, either  $C^8H^4 \begin{Bmatrix} CO - CO \\ CH^2.O.CO \end{Bmatrix}$ ,  $C^8H^4$ , or  $C^8H^4 \begin{Bmatrix} CH^2 - CO \\ CO.O.CO \end{Bmatrix}$ ,  $C^8H^4$ , which is probably formed by the action of diphtallic acid on diphtalyl:

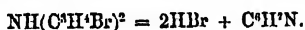


**PICOLINE**,  $C^8H^7N$ . On the occurrence of this base and its homologues in tobacco-smoke, see *Tobacco*.

Picoline is formed by heating allyl tribromide with ammonia, dibromallylamino being formed in the first instance, and subsequently resolved into hydrobromic acid and picoline (Ador & Baeyer, *Jahresb. f. Chem.* 1870, 807):



and



The formation of picoline from acrolein-ammonia is noticed in the 1st *Suppl.* (p. 944). According to Claus (*Ann. Ch. Pharm.* clviii. 222), it is not a direct product of the 'decomposition' of acrolein-ammonia, but results from the secondary decomposition of a non-volatile base, which is formed in the first instance and partly distils over unaltered.

**Oxidation-products.**—Picoline is not acted on by nitric or chromic acid, even at high temperatures, but permanganic acid and the potassium salt act upon it with considerable energy. When 150 grams of potassium permanganate, 25 grams of picoline, and  $1\frac{1}{2}$  litre of water were heated nearly to the boiling point in a flask with reversed condenser, a violent action took place, rendering it necessary to remove the source of heat; the reduction of the permanganate was completed in half an hour.

The products of this reaction are ammonia, probably a small quantity of pyridine, carbonic, nitric, acetic, oxalic, and a mixture of acids, amongst which dicarbo-pyridonic acid,  $C^8H^4N \begin{Bmatrix} CO^2H \\ CO^2H \end{Bmatrix}$ , predominates; this body, after several recrystallisations from water, was obtained in colourless plates resembling naphthalene. It is a bibasic acid; the neutral ammonium salt is extremely soluble in water; the acid salt is less soluble and crystallises in fine silky needles. The mercury, copper, cadmium, and zinc salts are also readily soluble. The barium and calcium salts, which are also soluble, were obtained in minute prismatic needles by adding the respective chlorides to a solution of the neutral sodium or ammonium salt. The silver salt is especially characteristic; it is obtained as a white gelatinous precipitate, insoluble in boiling water, and not visibly affected by exposure to light.

The oxidation of picoline likewise yields another acid of higher molecular weight, which still remains solid at  $220^\circ$  (Dewar, *Chem. News*, xxiii. 38).

Small quantities of picoline and its homologues have been found by Kramer & Pinner (*Deut. Chem. Ges. Ber.* iii. 75) in the 'first runnings' of spirit distillation.

**PICRIC ACID.** On the Thermic Relations of this compound, see *Heat* (p. 620).

**Detection in Beer.**—According to Sorby (*Qu. J. of Micros. Soc.* 1869, 358) picric acid may be very distinctly recognised in beer by means of its spectrum. The picric acid extracted by ether shows an absorption band at the blue end of the spectrum.

On the use of Picric Acid as a Precipitant for Alkaloids, see p. 43.

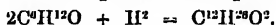
**PICROTOXIN.** According to J. Gaabe (*Russ. Zeitschr. Pharm.* x. 440, 461) picROTOXIN, treated with aqueous potash or baryta, yields compounds formed from it by addition of water and oxygen. The quantities of oxygen taken up varied in individual

experiments, and seemed to be greater the longer the mixtures of alkali and picrotoxin were heated in contact with the air. From the experiments of Barth (*1st. Suppl.* 643) and his own, Gaabe infers that picrotoxin is neither an acid nor a glucoside; and that it unites with bases only after having taken up water, or sometimes water and oxygen. Some of the experiments indicate the existence of acetyl-derivatives of picrotoxin and of its hydrates and oxygen-compounds.

**PINACOLIC ALCOHOL**,  $C^8H^{14}O = (CH^3)^2COH-CH(CH^3)^2$ , (Friedel a. Silva, *Compt. rend.* lxxvi. 226). This alcohol, isomeric with hexyl alcohol, is produced by treating pinacolin with sodium in presence of water, agitating the white substance thereby formed with water, and distilling the resulting liquid. Pinacolic alcohol then passes over as a liquid having a camphorous odour, boiling at  $120.5^\circ$ , and of sp. gr. 0.8347 at  $0^\circ$ . It solidifies at low temperatures to a mass of long silky needles melting at  $4^\circ$ . Treated with phosphorus iodide, or hydriodic acid, it yields the iodide,  $C^8H^{13}I$ , a liquid boiling at  $140^\circ-144^\circ$ , and having a sp. gr. of 1.4739 at  $0^\circ$ . Heated with water it partly decomposes, yielding a hexylene which boils at  $70^\circ$ . With silver acetate it yields pinacolic acetate, boiling at  $140^\circ-143^\circ$ , besides much hexylene. The chloride, obtained by the action of hydrochloric acid on the alcohol at  $100^\circ$  in closed tubes, boils at  $112.5^\circ-114.5^\circ$ , and has a density of 0.8891 at  $0^\circ$ .

By careful oxidation of the alcohol with potassium dichromate and sulphuric acid, pinacolin is reproduced. Pinacolin itself, when submitted to oxidation, yields a volatile crystalline acid melting at  $20^\circ$ .

The crystalline residue left in the retort after the removal of the pinacolic alcohol by distillation, melts at  $69^\circ$ , and is a pinacone of pinacolin:

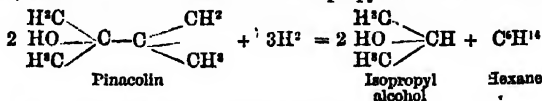


The molecular complication does not stop at pinacolin, so that by starting from acetone it may be possible to obtain a series of these compounds by successive duplication.

**PINACONE**,  $C^{12}H^{20}O^2$ . When hydriodic acid gas is passed over pinacone contained in a retort connected with a reversed condenser, the gas is absorbed, with great evolution of heat and liberation of iodine. The saturation is completed by gently warming the liquid; the contents of the retort are distilled; the distillate washed with aqueous potash and water—no organic acid being thereby dissolved; and the product is dried with phosphoric anhydride and distilled. The liquid begins to boil at  $40^\circ$ , impure isopropyl iodide passes over at  $88^\circ-96^\circ$ , and there remains only a very small quantity of a residue boiling at a higher temperature. By heating the crude isopropyl iodide for 16 hours with ten times its volume of water,  $\frac{1}{5}$ ths of it is dissolved, a heavy oil remaining undissolved. The aqueous solution contains isopropyl alcohol, which when separated and dried boils at  $80^\circ-82^\circ$ .

When the portion of the crude product of the action of hydriodic acid on pinacone which boiled below  $88^\circ$  was heated to  $100^\circ$  for sixteen hours with ten times its volume of water, a small quantity of a colourless very volatile hydrocarbon was obtained, which distilled between  $50^\circ$  and  $72^\circ$  (the greater part at  $70^\circ$ ), and gave by analysis numbers agreeing with the formula of hexane,  $C^6H^{14}$ .

It appears, then, that pinacone is converted by hydriodic acid (as by dilute acids) into pinacolin, which is further resolved into isopropyl alcohol and hexane:



(Linnemann, *Wien. Akad. Ber.* [2 Abth.] lxiii. 255).

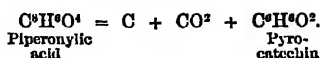
**PINOLIN**. A light oil obtained in the distillation of 'rosin-oil.'

**PIPERONAL**,  $C^8H^8O^2$ , and **PIPERONYLIC ACID**,  $C^8H^8O^4$ . These bodies, which stand to one another in the relation of aldehyde and acid, are formed by the oxidising action of potassium permanganate on piperic acid. They were first obtained by Fittig a. Mielek, who studied many of their properties and reactions, and the examination has been continued by Fittig a. Remsen. The principal results of these researches have been detailed in the First Supplement (pp. 947-949). The following are additional results obtained by Fittig a. Remsen (*Ann. Ch. Pharm.* clix. 129; *Chem. Soc. J.* [2], ix. 936).

*Action of Baryta-water, Hydrochloric acid and Water, on Piperonylic acid.*—A boiling aqueous solution of barium hydrate does not act on piperonylic acid. Dilute hydrochloric acid decomposes it at  $170^\circ$  into protocatechuic acid and free carbon:

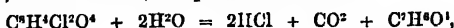


Water acts in a similar manner, but the decomposition does not take place below  $210^{\circ}$ , at which temperature the protocatechuic acid is resolved into carbon dioxide and pyrocatechuic acid:



In like manner piperonal heated to  $200^{\circ}$  with very dilute hydrochloric acid (10 or 12 vols. water to 1 vol. of the concentrated acid) is resolved into carbon and protocatechuic aldehyde:  $\text{C}^6\text{H}^4\text{O}^2 = \text{C} + \text{C}^6\text{H}^4\text{O}^2$ .

*Action of Phosphorus pentachloride on Piperonylic acid.*—The action is similar to that which takes place with piperonal (1st Suppl. 948). When 1 mol. piperonylic acid is heated with 3 mols.  $\text{PCl}_5$ , hydrochloric acid, phosphorus trichloride and oxychloride are formed, together with an oil which, when treated with water, yields dichloro-piperonylic acid,  $\text{C}^6\text{H}^3\text{Cl}_2\text{O}^4$ , and this when heated is completely resolved into hydrochloric acid, carbon dioxide, and protocatechuic acid:

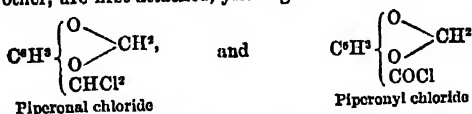


affording a proof that the compound formed in like manner from dichloropiperonal is really protocatechuic aldehyde.

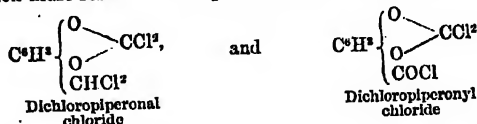
The experiments above mentioned, together with those described in the First Supplement, show that in piperonal the two oxygen-atoms not belonging to the aldehydic group, CHO, occupy a peculiar position, and that the formula previously assigned to this body must be rejected. The structural formulae of piperonal and piperonylic acid most in accordance with the reactions of these bodies are the following:



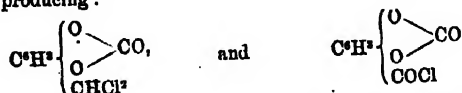
representing piperonal as the methylenic ether of protocatechuic aldehyde, and piperonylic acid as methylene-protocatechuic acid. When these bodies are subjected to the action of phosphorus pentachloride, the aldehyde-group, CHO, of the one, and the carboxyl of the other, are first attacked, yielding:



These bodies can lose no more oxygen by the action of pentachloride, and consequently any further action must result in the replacement of hydrogen by chlorine, producing:



which are exceptionally unstable bodies, the chlorine last introduced being analogous to that of carbonyl chloride,  $\text{COCl}^2$ . These compounds, in presence of water, exchange their  $\text{Cl}^2$  for O, producing:



which immediately split up on contact with water, yielding respectively protocatechuic aldehyde and protocatechuic acid.

*Synthesis of Piperonylic acid.*—That this acid really has the constitution of methylene-protocatechuic acid is proved by the fact that it may be formed synthetically by heating 1 mol. protocatechuic acid, 3 mols. potassium hydrate, and  $1\frac{1}{2}$  mol. methylene iodide in a sealed tube for several hours, first at the heat of the water-bath, and finally to  $140^{\circ}$  in an air-bath. On treating the nearly black contents of the tube with alcohol, heating the extract thus obtained with potash for some time to decompose any methylene-ether of the methylene-protocatechuic acid that may have formed, then adding hydrochloric acid, filtering from the brown amorphous precipitate thereby produced, and evaporating the filtrate, crystals are obtained which, after recrystallisation, treat-

ment with animal charcoal, and sublimation, exhibit the melting point ( $227^{\circ}$ ) and all the other characters of piperonylic acid (Fittig a. Remsen, *Zeitschr. f. Chem.* [2], vii. 289).

In a precisely similar manner ethylene-protocatechuic acid,  $C^6H^8 \begin{Bmatrix} O \\ \diagup \diagdown \\ O \end{Bmatrix} \begin{matrix} C^6H^4 \\ COOH \end{matrix}$ ,

may be prepared by heating protocatechuic acid with ethylene bromide and potassium hydrate (Fittig a. Macalpine, *ibid.* 291). See **PROTocatechuic Acid**.

**PITTICITE.** A specimen of this mineral from Rodruth in Cornwall, analysed by A. H. Church (*Chem. News*, xxiv. 99), exhibited the composition given under A; and, assuming that all the water driven off at  $100^{\circ}$  is hygroscopic, these numbers may be reduced by calculation to those under B:

	H <sup>2</sup> O at $103^{\circ}$	H <sup>2</sup> O at $175^{\circ}$	Loss by ignition	Fe <sup>2</sup> O <sup>3</sup>	As <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>2</sup>
A.	8.76	7.53	8.63	32.54	33.99	1.27	7.28 = 100
B.	—	17.71		35.67	37.25	1.39	7.98 = 100

W. Gümbel (*Münch. Akad. Ber.* 1870, i. 195) has analysed an iron sinter resembling pitticite, imbedded, in lumps of the size of a man's head and having a pitchy lustre, in a crumbling brown hæmatite which fills up a cleft in the fresh-water limestone in the Spitzberg in the Ries. From its mode of occurrence Gümbel infers that it has been deposited from a spring, and he remarks that arsenic is found in many vitreous deposits from still active springs. The deposit contained phosphoric acid and 2.28 p.c. calcium carbonate. A complete analysis by Putz gave:

As <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	CaO	MgO	BaO	H <sup>2</sup> O	X*	Y†
31.3	28.0	10.0	0.08	3.15	20.3	2.6	1.8 = 98.63

\* Insoluble in hydrochloric acid, amounting in some specimens to 6 p.c., and consisting chiefly of ferruginous clay. † Loss and CO<sup>2</sup>.

**PLATINUM.** *Fusibility.*—W. Skay (*Chem. News*, xxii. 268) observed that platinum in the form of fine wire may be fused in an ordinary blow-pipe flame if the loss of heat by conduction be prevented. E. J. Chapman (*ibid.* xxiii. 33) remarks that this fact has long been known, being mentioned in Plattner's 'Probirkunst,' p. 16, in Lenz's 'Lothrohrschule,' and Bruno-Kerl's 'Leitfaden.'

H. Violette (*Compt. rend.* lxxv. 1027) states that he has fused platinum in an ordinary furnace without the aid of a blast, and describes the furnace in which the fusion was effected. Dumas (*ibid.* 1028) suggests that the platinum may have contained traces of carbon, silicon, or sulphur, all which substances are known to lower its melting point considerably.

*Action of Hydrogen sulphide and Alkalis.*—Skay finds that platinum immersed in aqueous sulphydric acid or ammonium sulphide becomes covered, like gold (p. 573), with a layer of sulphide which protects it from the action of mercury; the film may, as also in the case of gold, be removed by chromic acid. Platinum, immersed in a solution of ammonia or a fused alkali, becomes coated with a film of oxide which likewise completely protects it from amalgamation.

*Platinum-Black.*—E. Smith (*American Chemist*, 1872, ii. 291) prepares platinum-black by reducing potassium platinochloride with hydrogen, dissolving out the potassium chloride with water, and drying the residue at a temperature not above  $100^{\circ}$ .

On the Separation of Platinum from Iridium, see **IRIDIUM** (p. 684).

On the Alloys of Platinum and Lead, see **LEAD** (p. 729).

**Chlorides.** According to Mather (*Sill. Am. J.* [2], xxxii. 262), *platinic chloride*, crystallised from aqueous solution, has the composition  $PtCl^4 + 10H^2O$ ; according to a more recent analysis by Bödecker (*Jahresb. f. Chem.* 1872, p. 277) it contains  $PtCl^4 + 8H^2O$ . H. Lawson (*Zeitschr. f. Chem.* [2], vii. 615) states that, according to analyses by Prottopow, the chloride separated in large prismatic crystals from an aqueous solution evaporating in the exsiccator, has the composition  $PtCl^4 + 10H^2O$ . It is remarkable that those crystals, in spite of their large amount of water, deliquesce very quickly on exposure to the air.

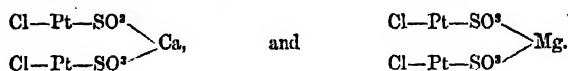
A new hydrate of platinic chloride is described by S. A. Norton (*J. pr. Chem.* [2], ii. 469). When 1 mol. platinic chloride in aqueous solution is mixed with a solution of 2 mols. silver nitrate, the double chloride  $AgCl.PtCl^4$ , described by Commaillé (1st Suppl. 652), separates out. The filtrate, which is free from silver, gives off acid on evaporation, and if then left over sulphuric acid, deposits large well-defined red crystals which appear to be monoclinic, and contain nothing but chlorine and platinum in the proportion to form the tetrachloride together with water. This hydrated chloride



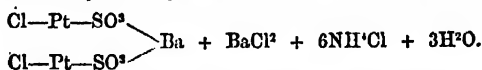
does not deliquesce in the air; when mixed with sal-ammoniac it gradually, after long standing or on heating, deposits ammonium platinochloride. It is not produced by evaporating a solution of platinic chloride containing excess of hydrochloric acid.

A compound of platinic chloride with *alcohol*,  $\text{PtCl}^{\text{Cl}}_2 \cdot 2\text{C}^{\text{H}}_2\text{O}$ , is obtained by evaporating a solution of the chloride in absolute alcohol in a dry vacuum. It then remains as a crystalline reddish-yellow mass, which is extremely deliquescent, and decomposes at  $60^\circ$  (Schützenberger, *Compt. rend.* lxx. 1134).

**Platosochlorosulphites** (Birnbaum, *Ann. Ch. Pharm.* clix. 116).—The formation of platosochlorosulphurous acid,  $\text{Pt}^{\text{Cl}} \left\{ \text{SO}^{\text{H}}_2 \right\}$ , by the action of sulphurous acid on ammonium platinochloride, is noticed in the 1st *Suppl.* (p. 1066), where also its ammonium and potassium salts are described. The *sodium salt*,  $\text{Pt}^{\text{Cl}} \left\{ \text{SO}^{\text{Na}}_2 \right\} \cdot 2\text{NH}^{\text{Cl}}_4 + \text{H}^{\text{O}}_2$ , obtained by neutralising the free acid with sodium carbonate, forms shining orange-coloured needles. The *calcium* and *magnesium salts*, prepared in like manner, are extremely deliquescent, so that they cannot be obtained in distinct crystals, but only as felted masses of fine needles. The magnesium salt especially has a beautiful satiny lustre. The analyses of these salts (disregarding accidental admixtures of  $\text{NH}^{\text{Cl}}_4$  and  $\text{H}^{\text{O}}_2$ ) led to the formulae:

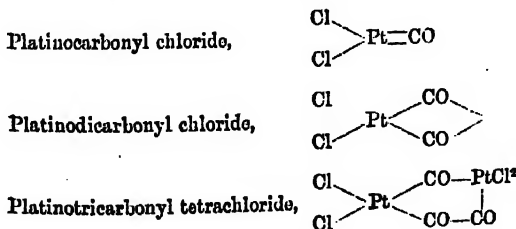


On neutralising the acid with caustic baryta, barium sulphite is first formed, and afterwards small reddish-yellow crystalline leaflets having the composition:



By acting on ammonium platinochloride or platosochlorosulphurous acid with acid ammonium sulphate, both the chlorine-atoms of platinum chloride may be replaced by the group  $\text{SO}^{\text{H}}_2$ . In the former case beautiful colourless prisms are obtained which, when neutralised with potassium carbonate, yield a salt having the composition  $\text{Pt}^{\text{Cl}} \left\{ \text{SO}^{\text{K}}_2 \right\} + \text{SO}^{\text{H}}_2 \left\{ \text{NH}^{\text{H}}_4 \right\} + 3\text{H}^{\text{O}}_2$ ; the original acid compound probably had the composition  $\text{Pt}^{\text{Cl}} \left\{ \text{SO}^{\text{H}}_2 \right\} + \text{SO}^{\text{H}}_2 \left\{ \text{NH}^{\text{H}}_4 \right\} + 4\text{H}^{\text{O}}_2$ , which indeed was confirmed by the platinum determination. The salt  $\text{Pt}(\text{SO}^{\text{H}}_2)_2 \cdot 2\text{NH}^{\text{H}}_4\text{Cl} + \text{H}^{\text{O}}_2$ , formerly described by Birnbaum (1st *Suppl.* 1066), he was not able to reproduce. By treating platosochlorosulphurous acid with acid ammonium sulphite, colourless prisms are obtained represented by the formula  $\text{Pt}(\text{SO}^{\text{H}}_2)_2 \cdot 2\text{NH}^{\text{H}}_4\text{Cl}$ , and agreeing very nearly in percentage composition with the salts formerly described. When sulphurous anhydride is passed for some time into an aqueous solution of ammonium platinochloride, and the liquid is neutralised with sodium carbonate, the salt,  $\text{SO}^{\text{Na}}_2\text{Pt} \cdot 3\text{SO}^{\text{Na}}_2$ , first described by Litton a. Schnederman (v. 540), is produced. Birnbaum regards this salt as  $\text{Pt}(\text{SO}^{\text{Na}}_2)_2 \cdot 3\text{SO}^{\text{Na}}_2$ .

**Platinocarbonyl Chlorides** (Schützenberger, *Ann. Chim. Phys.* [4], xxi. 350). Platinochloride unites with carbon monoxide, forming the following compounds:



When spongy platinum is heated to  $240^\circ$ – $250^\circ$  in a glass tube about half an inch wide, placed in an oil-bath, and dry chlorine is passed over it till it is wholly converted into dichloride, that is to say as long as the chlorine continues to be absorbed,

and the stream of chlorine is then replaced by carbon monoxide or a mixture of that gas with the dioxide, the cold part of the tube becomes coated with a mixture of the second and third compounds above mentioned, and from this mixture the pure compounds may be prepared.

**Platinocarbonyl Chloride**,  $\text{Cl}^1\text{Pt}^1\text{CO}$  (Schützenberger's *Carbonyl chloroplatinite*), is obtained by heating the crude product to  $150^\circ$ , the di- and tri-carbonyl compounds then giving off carbon monoxide. Heated to  $240^\circ$  in a stream of carbon dioxide, it sublimes in long golden-yellow needles which melt at  $195^\circ$  to a transparent orange-yellow liquid. It dissolves in hot carbon tetrachloride, and separates in needles on cooling. Water decomposes it into platinum, carbon monoxide, and hydrochloric acid, but the reaction is not definite, and part of the platinum remains in solution. With alcohol it yields ethylic chlorocarbonate. At  $300^\circ$ – $400^\circ$  it is resolved into platinum and carbonyl chloride, part of it, however, subliming undecomposed. Heated in a stream of carbon oxide to  $150^\circ$ , it is converted into platino-dicarbonyl chloride, and at  $250^\circ$  the tricarbonyl compound is also formed in considerable quantity.

**Platino-dicarbonyl Chloride**,  $\text{Cl}^1\text{Pt}^1\text{C}^2\text{O}^2$  (*Dicarbonyl chloroplatinite*), is obtained by heating the original crude product in a stream of carbon oxide to  $150^\circ$ . It sublimes slowly at that temperature in an atmosphere of the same gas, in white needles which melt at  $142^\circ$  to a yellow transparent liquid solidifying in long needles. It is decomposed by water into platinum, hydrochloric acid, carbon dioxide and carbon monoxide; gives off carbon monoxide at  $210^\circ$ , and is converted into platino-tricarbonyl tetrachloride; and when heated to  $150^\circ$  in a stream of chlorine, gives off carbonyl chloride, and yields a dark red liquid which solidifies at  $120^\circ$  to a red translucent amorphous mass containing 66.4 p.c. platinum and 22.4 chlorine.

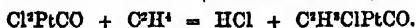
**Platino-tricarbonyl Tetrachloride**,  $\text{Cl}^1\text{Pt}^1\text{C}^3\text{O}^3$  (*Sesquicarbonyl chloroplatinite*).—This compound is obtained in the pure state when the crude product is treated with boiling carbon tetrachloride, and the first crystallisations are collected apart; it is much more soluble in that liquid than the dicarbonyl compound, and crystallises therefrom in slender yellow needles which melt at  $130^\circ$ , and are converted at  $250^\circ$ , with loss of carbon monoxide, into platinocarbonyl chloride,  $\text{Cl}^1\text{Pt}^1\text{CO}$ . Water and alcohol separate platinum from it, in the former case according to the equation:



Heated in an atmosphere of carbon monoxide, it is permanent, like the dicarbonyl compound, even at temperatures at which, in an indifferent gas, it would be converted into  $\text{Cl}^1\text{Pt}^1\text{CO}$ .

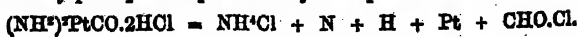
**Platino-ethylene-carbonyl Chloride**.—Ethylene-carbonyl chloroplatinite (*Chloroplatinite d'éthylène carbonyle*). When dry ethylene gas is passed over platino-monocarbonyl chloride heated to  $95^\circ$ , it is absorbed, and a yellow liquid is formed, probably having

the composition  $\text{Cl}^1\text{Pt}^1 \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}^2\text{H}^4 \end{matrix}$ . If the heat be raised a little above  $0^\circ$ , hydrochloric acid is formed, and at the end of the reaction there remains a dark-coloured product insoluble in water and not decomposed thereby. Its analysis led to the formula  $\text{C}^2\text{H}^4\text{Cl}^1\text{Pt}^1\text{CO}$ , whence it should be formed according to the equation:

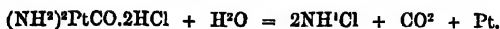


**Platinocarbonyl Diamines** (Schützenberger, *loc. cit.*) The mono- and di-carbonyl chlorides above described are attacked by dry ammonia even at ordinary temperatures, but the alteration is incomplete and merely superficial; if, however, the temperature be raised to the melting point, a thorough decomposition takes place, attended with formation of sal-ammoniac and separation of platinum. If the reaction be moderated by passing dry ammonia-gas into a solution of platinocarbonyl chloride in carbon tetrachloride, the liquid becomes decolorised and deposits light yellow flocks consisting of platinocarbonyl-diamine hydrochloride,  $(\text{NH}^4)^2\text{PtCO} \cdot 2\text{HCl}$ . Platino-dicarbonyl chloride, treated in a similar manner, yields platino-dicarbonyl-diamine hydrochloride,  $(\text{NH}^4)^2\text{PtC}^2\text{O}^2 \cdot 2\text{HCl}$ .

Both these compounds melt when heated, and are resolved into platinum, sal-ammoniac, nitrogen, hydrogen, and a pungent-smelling liquid which, when treated with water, yields hydrochloric acid and a volatile acid which reduces silver salts, and is therefore probably formic acid. Schützenberger supposes that the volatile liquid is formyl chloride,  $\text{CHO} \cdot \text{Cl}$ . It is produced in a small quantity only, and often does not appear at all, being resolved into hydrochloric acid and carbon monoxide. Its formation may perhaps be represented by the equation:



Water decomposes the hydrochloride of platinocarbonyl diamine, according to the equation:



**Phosphoplatinic Compounds** (Schützenberger, *Bull. Soc. Chim.* [2], xiv. 178; xvii. 482; xviii. 101, 148). Baudrimont observed that platinum is attacked at about  $200^\circ$  by phosphorus pentachloride, forming a brown substance which he regarded as a compound of phosphoric chloride and platonic chloride,  $2\text{PCl}_5 \cdot \text{PtCl}_4$  (iv. 512). Schützenberger, however, has shown that this body is really a compound of phosphorous chloride and platinous chloride, formed according to the equation:

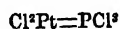


This compound, analogous in constitution to platinocarbonyl chloride,  $\text{PtCl}_2 \cdot \text{CO}$ , is capable, like the latter, of taking up diatomic groups such as  $\text{PCl}_3$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{Cl}_2$ , &c., and forming compounds such as  $\text{PtCl}_2 \cdot 2\text{PCl}_3$ ,  $\text{PtCl}_2 \cdot \text{PCl}_3 \cdot \text{CO}$ , &c.

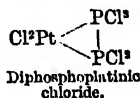
Schützenberger designates the compounds  $\text{PtCl}_2 \cdot \text{PCl}_3$  and  $\text{PtCl}_2 \cdot 2\text{PCl}_3$  as *phosphoplatinous chloride* and *phosphoplatinic chloride*; but as the platinum in both of them is tetravalent, it is better to name them *phosphoplatinic* and *diphosphoplatinic chloride*.

These two chlorides easily exchange the chlorine which is united to the phosphorus for hydroxyl, the first yielding a tribasic and the second a sexbasic acid; but the two chlorine-atoms united with the platinum resist the action of water, and behave like the chlorine of metallic chlorides, being replaceable by acid radicles.

In accordance with these facts the composition of these chlorides may be represented by the following structural formulæ, in both of which the platinum is quadrivalent and the phosphorus quinquivalent:



Phosphoplatinic  
chloride.



When phosphoplatinic chloride takes up a bivalent group, the double linking between the phosphorus and platinum is severed, the bivalent group thus introduced satisfying the platinum by one of its atomicities and the phosphorus by the other, e.g. in the formation of diphosphoplatinic chloride by addition of  $\text{PCl}_3$ .

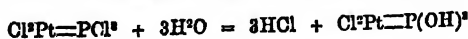
### *Monophosphoplatinic Compounds.*

**Chloride**,  $\text{Cl}^2\text{Pt}=\text{PCl}^3$ . This compound is formed by heating thoroughly dried spongy platinum and phosphorus pentachloride in molecular proportion to  $250^\circ$  in a long-necked flask, continuing the heat for half an hour after the first action is over, and then decanting the fused mass to separate a small quantity of uncombined platinum. On cooling, a red-brown crystalline mass is obtained made up of felted needles. If the liquid portion be decanted before the whole has solidified, the flask will be found lined with a druse of splendid large needles grouped in tufts. The compound may also be purified by crystallisation from chloroform or benzene.

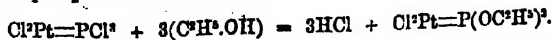
Phosphoplatinic chloride crystallises in beautiful maroon-coloured needles which melt at  $170^\circ$ , and dissolve with aid of heat in carbon tetrachloride, chloroform, benzene, and toluene, the last two liquids dissolving it in considerable quantity. When cautiously heated it is gradually resolved into platinous chloride and phosphorous chloride; when quickly heated it gives off phosphoric chloride and leaves a residuum of platinum, a small portion also volatilising unaltered.

Phosphoplatinic chloride gently heated in a stream of chlorine, takes up 2 atoms of chlorine, and forms a yellow powder which has the composition  $\text{Cl}^2\text{Pt}=\text{PCl}_4$ , and is resolved at a heat below  $200^\circ$  into phosphorus trichloride and platinum tetrachloride.

Phosphoplatinic chloride dissolves rapidly in water, forming a solution which contains hydrochloric acid and tribasic phosphoplatinic acid:



the water removing only three-fifths of the chlorine. *Alcohols* act in the same manner, forming phosphoplatinic ethers; e.g.



*Glycerin* is likewise attacked by phosphoplatinic chloride, with evolution of hydro-

chloric acid and formation of a syrupy substance soluble in water. With *acetic acid*, the products are acetyl chloride and phosphoplatinic acid :



*Ammonia and alcoholic amines* unite directly with phosphoplatinic chloride, forming complex bases which will be described further on.

Phosphoplatinic chloride unites directly with phosphorus trichloride, forming di-phosphoplatinic chloride,  $\text{Cl}^2\text{Pt}=\text{P}^2\text{Cl}^3$ .

**Phosphoplatinic Acid**,  $\text{Cl}^2\text{Pt}=\text{P}(\text{OH})^3$ . This tribasic acid is obtained by dissolving phosphoplatinic chloride in water, and evaporating the solution in a vacuum. It forms orange-red prismatic crystals, very deliquescent, and having a taste both acid and metallic. *Silver nitrate* produces in its solution a yellowish-white precipitate, not of constant composition, but probably containing  $\text{Cl}^2\text{Pt}=\text{P}(\text{OH})(\text{OAg})^2$ . With *neutral lead acetate* it gives a light yellow precipitate which, when washed with water and dried in a vacuum, contains  $(\text{Cl}^2\text{Pt}=\text{PO}^3)^2\text{Pb}^3 + 8\text{H}^2\text{O}$ ; it is decomposed by heat, giving off a considerable quantity of water. *Basic lead acetate* forms a yellow precipitate which has the composition  $(\text{Cl}^2\text{Pt}=\text{PO}^3)^2\text{Pb}^3.2\text{PbO} + 4\text{H}^2\text{O}$ , and detonates slightly when heated.

The *alkali salts* of phosphoplatinic acid have not been prepared; on saturating the acid with an alkali or alkali carbonate, the liquid quickly blackens, and on addition of alcohol yields a precipitate not containing chlorine.

**PHOSPHOPLATINIC ETHERS.** The *acid allyl ether*,  $\text{Cl}^2\text{Pt}=\text{P}(\text{OH})^2(\text{OC}^2\text{H}^3)$ , is formed by the action of allyl alcohol on the chloride; it is crystallisable and soluble in water.

**Amyl Phosphoplatinate.**—When 3 mols. amyl alcohol are added to a solution of 1 mol. phosphoplatinic chloride in benzene, and the product is washed with water and evaporated at a gentle heat, a thick highly coloured residue is left which does not crystallise. A similar product is obtained by treating the chloride directly with amyl alcohol. The viscid substance treated with ammonia yields a glutinous, yellow-brown insoluble mass, and a colourless solution which, on evaporation, leaves a hydrochloride crystallising in white nacrous leaflets; this salt is analogous to a diamylic ether, and contains  $(\text{C}^5\text{H}^{11}\text{O})^2(\text{OH})\text{P}=\text{Pt.N}^3\text{H}^4\text{Cl}$ .

**Ethyl Phosphoplatinate**,  $\text{Cl}^2\text{Pt}=\text{P}(\text{OC}^2\text{H}^3)^3$ .—Phosphoplatinic chloride dissolves in absolute alcohol, with rise of temperature and elimination of hydrochloric acid. On diluting with water and exactly neutralising the solution with sodium carbonate, a yellow crystalline mass separates which is easily purified by crystallisation from alcohol. It is better, however, to leave the alcoholic solution of the chloride to evaporate in a vacuum, wash the crystallised residu with water, and purify it by slow crystallisation from alcohol.

Ethyl phosphoplatinate forms large yellow triclinic prisms, insoluble in pure water, but soluble in water acidulated with hydrochloric acid, also in alcohol and in benzene. It melts at  $83^\circ$ , and decomposes at about  $180^\circ$ , giving off ethyl chloride, ethylene, hydrochloric acid, and, towards the end, marsh-gas and carbon monoxide, and leaving a grey residu containing platinum and metaphosphoric acid. Ethyl phosphoplatinate, treated in alcoholic solution with *silver nitrate*, exchanges part, or the whole, of its chlorine for the nitric residu  $\text{NO}^3$ , forming red syrupy uncrystallisable compounds represented by the formulæ:



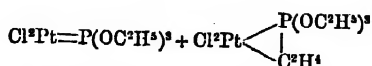
The alcoholic solution of ethyl phosphoplatinate immediately turns brown on addition of alcoholic potash-solution, depositing potassium chloride; and water added to the liquid throws down brown flocks which, in the dry state, take fire spontaneously in contact with the air; on redissolving these flocks in alcohol and evaporating the solution in a vacuum, a black amorphous mass is left possessing much greater stability. The analysis of this compound agrees approximately with the formula  $\text{PtPO}(\text{C}^2\text{H}^3\text{O})^2$ .

The alcoholic solution of ethyl phosphoplatinate, treated with *zinc* at common temperatures, turns brown, and yields, after some hours, on addition of water, a brown flocculent precipitate approximating in composition to the formula  $[\text{PtP}(\text{OC}^2\text{H}^3)^3]^2\text{Zn}$ . If the action of the zinc takes place at higher temperatures, an analogous compound is obtained having a darker colour, free from zinc, and agreeing approximately with the formula  $\text{PtP}^2(\text{OC}^2\text{H}^3)^3$ .

Ethyl phosphoplatinate unites directly with *phosphorus trichloride*, the combination being attended with evolution of heat, and resulting in the formation of ethyl di-phosphoplatinate,  $\text{Cl}^2\text{Pt}=\text{P}^2\text{Cl}^3(\text{OC}^2\text{H}^3)^3$ .

An alcoholic solution of ethyl chloroplatinate saturated with *ethylene* yields, after

evaporation of the alcohol, a light yellow oily liquid insoluble in alcohol, and having the composition :

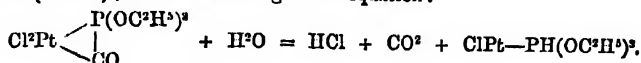


This additive compound gives off its ethylene in contact with phosphorous chloride or ammonia.

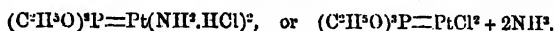
Ethyl phosphoplatinate likewise unites directly with carbon monoxide when this gas is passed into its solution in anhydrous ether, yielding a light yellow oily compound

having the composition  $\text{Cl}^2\text{Pt} \begin{array}{c} \text{P}(\text{OC}^2\text{H}^5)^3 \\ | \\ \text{CO} \end{array}$ . This compound is soluble in alcohol,

ether, and benzene, but insoluble in water, and decomposes gradually in contact with water, yielding carbonic and hydrochloric acids, together with a yellow viscous body,  $\text{ClPt}-\text{PH}(\text{OC}^2\text{H}^5)^3$ , formed according to the equation :

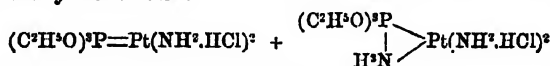


*Action of Ammonia on Ethyl Phosphoplatinate.*—This ether combines directly with ammonia, forming bases of complex constitution. Its solution in ammonia yields, by evaporation, colourless deliquescent prismatic crystals of a salt very soluble in water and in alcohol. The same salt is more easily obtained by passing ammonia gas into a solution of ethyl phosphoplatinate in benzene, the liquid after a while solidifying to a mass of white crystals. This salt is the hydrochloride of a diamine, containing:



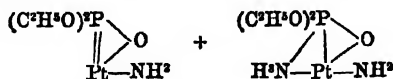
The *platinohydrochloride* of the same base is a light yellow precipitate which dissolves in hot water and crystallises on cooling in yellow prisms having the composition  $(\text{C}^2\text{H}^5\text{O})^3\text{P}=\text{Pt}(\text{NH}^2.\text{HCl})^2.\text{PtCl}^4$ .

When a solution of ethyl phosphoplatinate in absolute alcohol is saturated with ammonia gas, the liquid becomes colourless, and gradually deposits colourless crystals less deliquescent than the former. The compound thus formed is a complex double salt represented by the formula :



the first term of which is the hydrochloride above described.

This double hydrochloride, treated with strong aqueous potash, gives off ethylamine, and yields an oily product which, under the influence of very strong potash, is transformed by simple dehydration into a crystalline mass. This product is soluble in pure water and in alcohol, but very slightly soluble in potash-ley. Its solution evaporated over the water-bath leaves an amorphous colourless transparent residue, having the composition :



This substance is probably a mixture of two bases differing from the original alkaloids by containing a molecule less of ethylamine.

The double hydrochloride above mentioned melts at  $150^\circ$ , and decomposes, giving off ammonia and ethyl chloride, and leaving a brittle, vitreous, colourless, transparent mass, very soluble in water and in alcohol. This body, which has the composition  $(\text{C}^2\text{H}^5\text{O})^3\text{P}=\text{PtON}^2\text{H}^2\text{Cl}$ , may be regarded as the monohydrochloride of a diamine, or as the hydrochloride of an ammoniated monamine, viz. :



The chloroplatinate is a yellow precipitate containing 48.5 p.c. platinum, which agrees with the preceding formulæ.

On attempting to crystallise this body from boiling water, or on adding chlorine or a large excess of platinic chloride to the solution of the vitreous salt, a crystalline,

slightly yellowish deposit is obtained, which dissolves in boiling water, and crystallises therefrom in light yellow needles. This compound, which contains neither carbon nor phosphorus, is represented by the formula :



Ethyl phosphoplatinate combines also with solid *toluidine*. When an alcoholic solution of the ether is heated with an excess of this base, the liquid becomes decolorised, and yields on cooling a crystalline deposit which, when washed with dilute hydrochloric acid and repeatedly crystallised from boiling alcohol, yields colourless prismatic needles easily soluble in alcohol, very slightly soluble in water and in ether, and having the composition  $(\text{C}^2\text{H}_5\text{O})_2\text{P}(\text{C}^2\text{H}_5\text{N})\text{PtCl}_2$ . This compound, treated in alcoholic solution with potash, yields potassium chloride and a colourless product which crystallises in fine silky needles insoluble in water, and less soluble in alcohol than the preceding. Dried at  $100^\circ$  it has the composition  $(\text{C}^2\text{H}_5\text{O})_2\text{P}(\text{C}^2\text{H}_5\text{N})\text{Pt}(\text{OH})_2$ .

**Methyl Phosphoplatinate**,  $\text{Cl}_2\text{Pt}=\text{P}(\text{OCH}_3)_2$ .—Phosphoplatinic chloride acts strongly on methyl alcohol; and the resulting liquid evaporated in a vacuum yields a crystalline mass which may be purified by repeated crystallisation from alcohol, or by solution in benzene. The methylic ether separates by slow evaporation in slender orange-yellow needles, slightly soluble in pure water, soluble in water containing hydrochloric acid, also in alcohol, ether, and benzene; it melts and decomposes when heated.

### Diphosphoplatinic Compounds.

**Chloride**,  $\text{Cl}_2\text{Pt} \begin{matrix} \nearrow \text{PCl}_3 \\ \searrow \text{PCl}_3 \end{matrix}$ .—This compound is easily prepared by dissolving phosphoplatinic chloride, with aid of heat, in excess of phosphorus trichloride. The solution on cooling deposits crystals which may be washed with a small quantity of benzene or chloroform, and desiccated at  $100^\circ$  in dry air. Or phosphorus trichloride may be added in equivalent proportion to a solution of phosphoplatinic chloride in benzene, the diphosphoplatinic chloride then crystallising out on cooling. Lastly it is formed, with evolution of carbon monoxide, by the action of phosphorus trichloride on either of the platinumcarbonyl chlorides,  $\text{Cl}_2\text{Pt}=\text{CO}$  or  $\text{Cl}_2\text{Pt}=\text{C}^2\text{O}^2$  (p. 985).

Diphosphoplatinic chloride forms beautiful canary-yellow crystals arranged in funnel-shaped groups with rectangular section. It melts at  $160^\circ$ , and decomposes at a higher temperature, giving off phosphorus trichloride. It dissolves in phosphorus trichloride, carbon tetrachloride, chloroform, benzene, and toluene. Water attacks it strongly, eliminating hydrochloric acid and forming diphosphoplatinic acid :



If the temperature rises during the reaction, another acid is obtained having the composition  $\text{ClPtP}^2\text{O}(\text{OH})_5$ , and derived from the former by loss of a molecule of hydrogen chloride (*infra*).

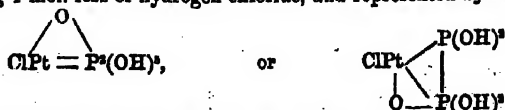
*Ethylic alcohol* and *methylic alcohol* dissolve the chloride, forming the corresponding ethers, e.g. :



*Amylic alcohol* reacts in a similar manner. With *glycerin*, hydrogen chloride is evolved, and a thick, nearly colourless mass is formed.

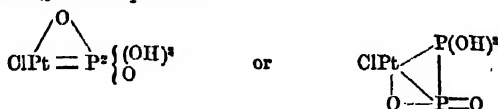
**Diphosphoplatinic Acid**,  $\text{Cl}_2\text{Pt}=\text{P}^2(\text{OH})_6$ , or  $\text{Cl}_2\text{Pt} \begin{matrix} \nearrow \text{P}(\text{OH})_3 \\ \searrow \text{P}(\text{OH})_3 \end{matrix}$ . The preparation of this compound succeeds only at a low winter temperature. Diphosphoplatinic chloride is exposed to moist air, and as soon as it has deliquesced, the light yellow syrupy liquid is evaporated, also at a low temperature. The diphosphoplatinic acid is thus obtained in light yellow extremely deliquescent needles.

If during this operation the temperature rises to  $10^\circ$  or  $12^\circ$ , a colourless crystallisable acid is obtained, less deliquescent than diphosphoplatinic acid, differing from it by containing 1 mol. less of hydrogen chloride, and represented by the formula :



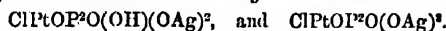
This acid is much more stable than diphosphoplatinic acid. When heated to  $150^\circ$ ,

it gives off water and is converted into a light yellow non-deliquescent powder, soluble in water, and having the composition:



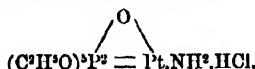
The solution of the acid,  $\text{ClPtOP}^2(\text{OH})^2$ , gives, with silver nitrate, a white, slightly yellowish precipitate containing 6.83 P, 2.19 Cl, 23.33 Pt, and 51.25 Ag, numbers agreeing nearly with the formula  $\text{ClPtOP}^2(\text{OH})(\text{OAg})^2$ , supposing half the chlorine to be replaced by the residue  $\text{NO}^2$ . The precipitate in question is probably a mixture of two salts.

The acid dehydrated at  $150^\circ$  forms with silver nitrate an analogous precipitate containing 5.5 Cl and 41.8 Ag, numbers which agree with the composition of a mixture in equivalent proportions of the *di-* and *tri-argentic* salts:



**Ethyl Diphosphoplatinate.**  $\text{Cl}^2\text{Pt} = \text{Pt}^2(\text{OC}^2\text{H}^5)^2$ , is easily formed by the action of absolute alcohol on diphosphoplatinic chloride. Water added to the resulting solution separates a light yellow oil which, when cooled to a low temperature, solidifies to a mass of prismatic crystals (mono- or tri-clinic). This ether sometimes remains for a long time in a state of supersaturation. When decomposed by heat it yields ethylene, ethyl chloride, platinum and phosphoric acid.

Ethyl diphosphoplatinate dissolves in aqueous ammonia, and the solution, evaporated in a vacuum, leaves a white crystalline mass, deliquescent and soluble in alcohol. The body thus formed is the hydrochloride of a monamine:



derived, not from ethylic diphosphoplatinate, but from a compound containing 1 mol. less of ethyl chloride.

**Platinum Iodides.** Topsoë (*Chem. Centr.* 1870, 683) confirms the observation made by Clementi (*Cimento*, ii. 192) that the platonic iodide prepared by precipitating platonic chloride with potassium iodide (iv. 671) contains excess of platinum, and adds that it is obtained in greater purity by the action of hydriodic acid on platonic chloride at ordinary temperatures. It gives off iodine at  $130^\circ$ . It dissolves in hydriodic acid and in solutions of metallic iodides, forming dark crimson solutions. Many of the double iodides are, however, more readily obtained by mixing solutions of metallic iodides with platonic chloride, and leaving them to crystallise. They have a brown colour, and metallic lustre, and their solutions deposit platonic iodide on standing, and more quickly on boiling. Sulphurous acid and alkaline sulphites decolorise their solutions, forming platinous sulphite.

**Hydroplatonic Iodide**,  $\text{PtI}^4 \cdot 2\text{HI} + 9\text{H}^2\text{O}$ , forms large monoclinic deliquescent crystals. **Potassio- and Ammonio-platonic iodides** are anhydrous, and crystallise in the monoclinic system. **Sodio-platonic iodide**,  $\text{PtI}^4 \cdot 2\text{NaI} + 6\text{H}^2\text{O}$ , is monoclinic. The **calcium salt**,  $\text{PtI}^4 \cdot \text{CaI}^2 + 12\text{H}^2\text{O}$ , crystallises in rhombohedrons of  $106^\circ 31'$  in combination with an acute rhombohedron. The compounds of platonic iodide with the iodides of **magnesium, manganese, zinc, iron, cobalt, and nickel**, are represented by the general formula  $\text{PtI}^4 \cdot \text{RI}^2 + 9\text{H}^2\text{O}$ , and crystallise in hexagonal prisms combined with a rhombohedron of  $76^\circ 17'$  to  $76^\circ 27'$ . At a higher temperature a **nickel salt**,  $\text{PtI}^4 \cdot \text{NiI}^2 + 6\text{H}^2\text{O}$ , crystallises in hexagonal prisms with a rhombohedron of  $127^\circ 40'$ .

**Platonic Oxide.** Topsoë finds that the hydrated platonic oxide prepared by Dübrenin's method, of evaporating a solution of platonic chloride with excess of sodium carbonate, and treating the residual mass suspended in water with acetic acid, is identical with that which Wittstein obtained by precipitating platonic nitrate with calcium carbonate (iv. 671), and has the composition  $\text{PtO}^2 + 2\text{H}^2\text{O}$ . Frémy's **platonic acid** (*Ann. Chim. Phys.* [3], xxxi. 478), prepared by boiling platonic chloride with a very large excess of sodium carbonate, and decomposing the resulting sodium platinate with acetic acid, and easily soluble in dilute acids, even in acetic acid, has, when dried over calcium chloride, the composition  $\text{PtO}^2 + 4\text{H}^2\text{O}$ , and gives off 2 mols.  $\text{H}^2\text{O}$  at  $100^\circ$ .

**Platinates of Barium and Calcium.**—By boiling a solution of platonic chloride with a quantity of baryta-water sufficient to render the liquid alkaline after boiling, Topsoë (*Zeitschr. f. Chem.* 1870, 682) obtained from dilute solutions yellowish-white scales having a silky lustre, and from concentrated solutions a dense straw-yellow precipi-

tate made up of feathery and stellate groups of microscopic crystals. This precipitate is extremely difficult of solution in water, baryta, and soda, easily soluble in dilute acids, with the exception of cold acetic acid; hot acetic acid separates platonic oxide from it. According to Topsoë's analysis this compound consists of barium platinate,  $\text{BaPtO}_3 + 4\text{H}_2\text{O}$ , and gives off 3 mols. (about 10 p.c.) water at about  $300^\circ$ . When an insufficient quantity of baryta is used, so that the liquid, after boiling, has a neutral or acid reaction, precipitates are obtained which must be regarded as mixtures or loose combinations of platonic acid with barium platinate (Topsoë). According to Johannsen, on the other hand (*Ann. Chem. Pharm.* clv. 204), the precipitates obtained by boiling platonic chloride with baryta-water all contain chlorine, the yellow precipitate formed when the baryta is in excess containing, according to eight analyses, 42.71-43.68 p.c. Pt, 4.75-6.44 Cl, 33.18-34.26 BaO, and 10.92-11.58  $\text{H}_2\text{O}$ ; with excess of platonic chloride the precipitate is richer in platinum and chlorine, poorer in water and baryta. Johannsen also finds that a solution of platonic chloride mixed with excess of baryta-water, and exposed to sunshine, immediately deposits a pure yellow precipitate which, in diffused light, forms more slowly and separates in hard warty crystals; analysis gave the atomic relation  $4\text{Pt} : 4\text{Ba} : 4\text{Cl} : 10\text{O} : 11\text{H}_2\text{O}$ . With excess of platonic chloride there is formed a darker-coloured salt exhibiting the atomic relation  $5\text{Pt} : 5\text{Ba} : 6\text{Cl} : 12\text{O} : 13\text{H}_2\text{O}$ .

To prepare Herschel's 'sun-salt' (iv. 672), Johannsen used an excess of lime-water more than sufficient to precipitate all the platinum, and obtained a nearly white salt of constant composition, answering to the atomic relation,  $2\text{Pt} : 2\text{Ca} : 2\text{Cl} : 5\text{O} : 7\text{H}_2\text{O}$ . On heating platonic chloride with lime-water, precipitates are formed richer in platinum and chlorine, and poorer in lime and water in proportion as the excess of platonic chloride used is greater. Whether the chlorine in these compounds is directly associated with the platinum or with the barium or calcium has not yet been determined (Johannsen, *loc. cit.*)

**PLATINUM-COMPOUNDS, AMMONIACAL.** A large number of new compounds belonging to this class have been prepared by Cleve (*Bull. Soc. Chim.* [2], vii. 12; xv. 161; xvi. 203; xvii. 289; *Deut. Chem. Ges. Ber.* iv. 70, 673; vi. 1469; *Svenska Vetenskaps Akademiens Handlingar*, 1872, x. No. 9), and a new theory of their constitution, founded in great part on Cleve's researches, has been proposed by Blomstrand (*Deut. Chem. Ges. Ber.* iv. 40; *Chem. Soc. J.* [2], ix. 189).

The platinum in some of these compounds is bivalent (*plato* or *platoso*), and exchanges two of its combining units with the bivalent groups  $\text{NH}_2$  or  $\text{N}^2\text{H}_2$ , each of which retains one combining unit free. In others the platinum is quadrivalent (*platino*), and exchanges some of its combining units with ammonia or diammonia, the remaining units being satisfied by combination with electro-negative radicles. In others, again, the platinum accumulates in such a manner as to form compounds containing  $(\text{Pt}^2)^2$ ,  $(\text{Pt}^2-\text{Pt}^2)^2$ ,  $(\text{Pt}^2-\text{Pt}^2-\text{Pt}^2-\text{Pt}^2)^2$ , &c. The bivalent groups  $\text{NH}_2$ ,  $\text{N}^2\text{H}_2$ , always go by pairs, excepting in the semi-diammoniums, in which half or a quarter of the combining units of the platinum is satisfied by once  $\text{N}^2\text{H}_2$ .

The names and constitution of the several groups are given in the following table, the unsaturated combining units being denoted by dashes:

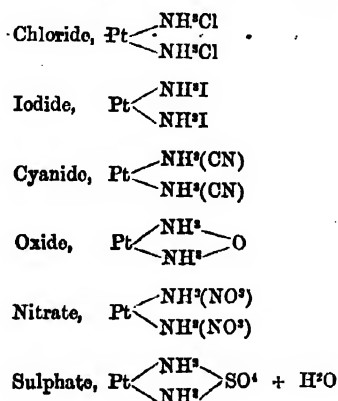
1. Platosammonium (Reiset's second base)	. . . . .	$\text{Pt}^2 \left\{ \begin{array}{l} \text{NH}^2- \\ \text{NH}^2- \end{array} \right.$
2. Platosemidiammonium	. . . . .	$\text{Pt}^2 \left\{ \begin{array}{l} \text{NH}^2(\text{NH}^2)- \\ - \end{array} \right.$
3. Platosomonodiammonium	. . . . .	$\text{Pt}^2 \left\{ \begin{array}{l} \text{NH}^2(\text{NH}^2)- \\ \text{NH}^2- \end{array} \right.$
4. Platosodiammonium (Reiset's first base)	. . . . .	$\text{Pt}^2 \left\{ \begin{array}{l} \text{NH}^2(\text{NH}^2)- \\ \text{NH}^2(\text{NH}^2)- \end{array} \right.$
5. Platinammonium (Gerhardt's base)	. . . . .	$=\text{Pt}^4 \left\{ \begin{array}{l} \text{NH}^2- \\ \text{NH}^2- \end{array} \right.$
6. Platinosemidiammonium	. . . . .	$=\text{Pt}^4 \left\{ \begin{array}{l} \text{NH}^2(\text{NH}^2)- \\ - \end{array} \right.$
7. Platinomonodiammonium	. . . . .	$=\text{Pt}^4 \left\{ \begin{array}{l} \text{NH}^2(\text{NH}^2)- \\ \text{NH}^2- \end{array} \right.$
8. Platinodiammonium (radicle of Gros' and Raewsky's bases)	. . . . .	$=\text{Pt}^4 \left\{ \begin{array}{l} \text{NH}^2(\text{NH}^2)- \\ \text{NH}^2(\text{NH}^2)- \end{array} \right.$
9. Diplatinammonium	. . . . .	$=(\text{Pt}^2)^2 \left\{ \begin{array}{l} \text{NH}^2- \\ \text{NH}^2- \\ \text{NH}^2- \\ \text{NH}^2- \end{array} \right.$



10. Diplatoso-diammonium . . . . .  $(Pt^2)^+ \begin{Bmatrix} NH^2(NH^4) \\ NH^2(NH^4) \end{Bmatrix}$   
 11. Diplatinodiammonium . . . . .  $\equiv (Pt^2)^+ \begin{Bmatrix} NH^2(NH^4) \\ NH^2(NH^4) \end{Bmatrix}$   
 12. Diplatinotetradiammonium . . . . .  $\equiv (Pt^2)^+ \begin{Bmatrix} NH^2(NH^4) \\ NH^2(NH^4) \\ NH^2(NH^4) \\ NH^2(NH^4) \end{Bmatrix}$

The following is an enumeration of all the ammoniacal platinum-compounds at present known. Some have been already described (iv. 673-678, and 1st Suppl. 952-955); and of these only the names and formulæ are here given. The rest, nearly all of which have been discovered by Cleve, will be shortly described.

1. **Platosammonium Compounds**,  $Pt^+ \begin{Bmatrix} NH^2R \\ NH^2R \end{Bmatrix}$  (R in this and all the following formulæ denoting an electro-negative univalent radicle).



**Bromide**,  $PtN^2H^4Br^2$ .—Crystalline, very slightly soluble precipitate obtained by double decomposition with the nitrate.

**Platocyanide**,  $PtN^2H^4(CN)^2.Pt^+$ .—Orange-coloured, amorphous precipitate.

**Sulphocyanate**,  $PtN^2H^4(CNS)^2$ .—Thin yellow crystals. Its solution gives with silver nitrate a yellow precipitate containing  $PtN^2H^4Ag^4(CNS)^6$ . Yellow crystals, isomeric with those just mentioned, are obtained on adding ammonia to a solution of potassium platosulphocyanate.

**Nitrite**,  $Pt^+N^2H^4(NO^2)^2$ .—Obtained by double decomposition. It is a white crystalline powder, very slightly soluble in cold water, easily soluble in boiling water. Decomposes violently when heated. Nitric acid converts it into nitroso-nitrate of platinumammonium,  $(NO^2)^2Pt^+(N^2H^4)(NO^2)^2$ . It unites with chlorine and bromine, forming the bromo- and chloro-nitrites of platinumammonium, e.g.  $Cl^2Pt^+(N^2H^4)(NO^2)^2$ .

**Sulphite**,  $PtN^2H^4CO^2$ .—Obtained by passing sulphur dioxide into a boiling solution of the nitrite. The solution, which at first turns green, is filtered as soon as it becomes colourless, and evaporated over the water-bath, and the residue, after washing with alcohol, is redissolved in water. The solution yields by spontaneous evaporation delicate colourless crystals.

**Chlorosulphite**,  $PtN^2H^4(SO^2H)Cl$ .—Obtained in needles by treating a boiling solution of platosammonium chloride with sulphurous acid, and leaving it to evaporate. Peyrone, by treating the chloride with ammonium sulphite, obtained a compound probably containing  $PtN^2H^4(SO^2NH^4)Cl$ .

**Double Sulphites**.—These salts are analogous to the unknown acid sulphite,  $PtN^2H^4(SO^2H)^2$ . Peyrone obtained the ammonium salt by treating the chloride with

ammonium sulphite in excess. It forms colourless, well-defined crystals. The following salts are obtained from it by double decomposition (Cleve):—

Silver salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Ag} + \text{H}_2\text{O}$	White crystalline powder
Barium salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Ba}$	Crystalline powder
Manganous salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Mn}$	Dense crystalline precipitate
Zinc salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Zn} + 6\text{H}_2\text{O}$	Flattened microscopic prisms
Nickel salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Ni} + 7\text{H}_2\text{O}$	Bluish crystalline powder, which does not give off its water at $100^\circ$
Cobalt salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Co} + 6\text{H}_2\text{O}$	Small rose-coloured crystals
Cupric salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2\text{Cu} + 5\text{H}_2\text{O}$	Bluish-green flattened prisms
Uranyl salt,	$\text{PtN}^{\text{H}}\text{H}^{\text{H}}(\text{SO}_3)_2(\text{UO}_2)^{\text{H}} + 2\text{H}_2\text{O}$	Yellow crystalline powder, giving off $1\text{H}_2\text{O}$ at $100^\circ$
Lead salt		Amorphous precipitate

2. **Platosemidiammonium Compounds**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}}\text{R} \\ \text{R} \end{smallmatrix}\right.$ . These compounds, isomeric with the platossammonium compounds, are formed by addition of ammonia to a platinous salt, whereas the platossammonium salts are formed by abstraction of ammonia from the platossodiammonium (tetrammonio-platinous) compounds (iv. 673).

**Chloride**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}}\text{Cl} \\ \text{Cl} \end{smallmatrix}\right.$ . This is the yellow salt, isomeric with platossammonium chloride (Reisot's salt), and with the green salt of Magnus (iv. 674), which Peyrone obtained by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, filtering after 24 hours, and treating the yellowish-green residue with boiling water, which dissolves the yellow and leaves the green salt formed at the same time. The solution on cooling deposits the platosemidiammonium salt in small yellow prisms, which appear to differ in form from platossammonium chloride. They are more soluble, requiring only 387 pts. of cold and 26 pts. of boiling water. This salt is decomposed by silver salts, yielding corresponding salts of platosemidiammonium. Soda removes hydrochloric acid from it, leaving a dingy-coloured powder which probably has the composition  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{OH}^{\text{H}} \\ \text{N}^{\text{H}}\text{H}^{\text{H}} \end{smallmatrix}\right. + \text{H}_2\text{O}$  (Cleve).

**Bromide**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}}\text{Br} \\ \text{Br} \end{smallmatrix}\right.$ .—Obtained on adding hydrobromic acid to the solution of the corresponding nitrate, in bulky yellow needles, quickly changing to a brick-red crystalline mass, which, by recrystallisation from boiling water, is again converted into yellow crystals.

The **iodide** crystallises in slender yellow needles. It unites with iodine to form a black periodide.

**Cyanide**.—Colourless needles. The **platinocyanide**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}}\text{Cy} \\ \text{Cy} \end{smallmatrix}\right.$ ,  $\text{PtCy}_2 + 3\text{H}_2\text{O}$ , is a sulphur-yellow powder.

The **sulphocyanate**, isomeric with Buckton's platossammonium sulphocyanate (v. 513), forms golden-yellow flattened prisms, the solution of which is decomposed on boiling. It appears to react with nitromuriatic acid differently from the isomeric platossammonium sulphocyanate.

The **nitrate**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}}(\text{NO}_3) \\ (\text{NO}_3) \end{smallmatrix}\right.$ , obtained by decomposing the chloride with silver nitrate, forms whitish crusts made up of ill-defined crystals. Its solution mixed with hydrochloric acid deposits the corresponding chloride.

**Nitrite**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}}(\text{NO}_2) \\ (\text{NO}_2) \end{smallmatrix}\right.$ .—Lang obtained this salt by adding ammonia to platinous nitrite. It may also be prepared by double decomposition. It forms long silk needles which detonate when heated. Hot hydrochloric acid converts it into the corresponding chloride. Sulphurous acid converts it into an amorphous substance (Cleve).

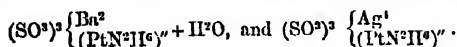
**Sulphate**,  $\text{Pt}^{\text{H}}\left\{\begin{smallmatrix} \text{N}^{\text{H}}\text{H}^{\text{H}} \\ \text{SO}_4 \end{smallmatrix}\right.$ .—Yellowish-white crystalline crusts.

**Chlorosulphite**,  $\text{Pt} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4\text{Cl} \\ \text{SO}^2\text{H} \end{smallmatrix} \right\}$ .—Colourless, moderately soluble needles, obtained by passing a current of sulphur dioxide through a boiling solution of the chloride, and evaporating over the water-bath.

**Double Sulphites**.—The ammonium salt,  $(\text{SO}^2)^2 \left\{ \begin{smallmatrix} (\text{NH}^4)^4 \\ (\text{PtN}^2\text{H}^4)^2 \end{smallmatrix} \right\}$ , is obtained by dissolving the chloride in excess of ammonium sulphate. On adding alcohol the salt is precipitated in oily drops which soon crystallise. By recrystallisation it is obtained in slender needles.

The chlorinated ammonium sulphite,  $(\text{SO}^2)^2 \left\{ \begin{smallmatrix} (\text{NH}^4)^2 \\ (\text{PtN}^2\text{H}^4\text{Cl})^2 \\ (\text{PtN}^2\text{H}^4)^2 \end{smallmatrix} \right\}$ , is prepared like the preceding, excepting that the chloride must be kept in excess. It forms bulky, prismatic, very soluble crystals (Peyrono; Clevo).

The ammonium salt forms with barium and silver salts precipitates containing—



**Oxalates**.—The neutral oxalate obtained by the action of ammonium oxalate on platosemidiammonium nitrate forms colourless microscopic crystals containing—



### 3. Platosemonodiammonium Compounds, $\text{Pt}^{\text{R}} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4\text{R} \\ \text{NH}^4\text{R} \end{smallmatrix} \right\}$ , or $(\text{N}^2\text{H}^4\text{Pt}) \left\{ \begin{smallmatrix} \text{H}^4 \\ \text{H}^4 \end{smallmatrix} \right\} \text{N}^2\text{R}$

**Chloride**,  $\text{Pt} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4\text{Cl} \\ \text{NH}^4\text{Cl} \end{smallmatrix} \right\}$ .—Very soluble colourless needles or nacreous scales, obtained by the action of hydrochloric acid on the nitrate. Its solution mixed with potassium chloroplatinite yields the following salt:

**Chloroplatinite**,  $2 \left[ \text{Pt}^{\text{R}} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4\text{Cl} \\ \text{NH}^4\text{Cl} \end{smallmatrix} \right\} \right]. \text{Pt}^{\text{R}}\text{Cl}^2$ .—This salt, polymeric with platosemonodiammonium chloride,  $[=3\text{PtN}^2\text{H}^4\text{Cl}^2]$ , constitutes the brown-red salt described by Peyrono (iv. 674). It is always formed in small quantity when ammonia is added to platinumous chloride. It is slightly soluble in cold, more soluble in boiling water. Treated with silver nitrate it yields silver chloroplatinite and platosemonodiammonium nitrate; with potassium permanganate and hydrochloric acid it yields rhombic tables of platosemonodiammonium chloride.

**Nitrate**,  $\text{Pt} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4(\text{NO}^3) \\ \text{NH}^4(\text{NO}^3) \end{smallmatrix} \right\}$ .—Ill-defined crystals, grouped in yellowish crusts; very soluble, and decomposing with violence when heated.

**Sulphate**,  $\text{Pt} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4 \\ \text{NH}^4 \end{smallmatrix} \right\} \text{SO}^4$ .—Moderately soluble snow-white crusts.

### 4. Platosediammonium Compounds, $\text{Pt}^{\text{R}} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^4\text{R} \\ \text{N}^2\text{H}^4\text{R} \end{smallmatrix} \right\}$ , or $\text{N}^2 \left\{ \begin{smallmatrix} \text{H}^4 \\ \text{N}^2\text{H}^4\text{Pt}^{\text{R}} \end{smallmatrix} \right\} \text{R}^2$

This group includes Reiset's first chloride (tetrammonio-platinous chloride, iv. 675), and its analogues. The chloride, treated with a solution of potassium chloroplatinite, yields the chloroplatinite of the series, which is the green salt of Magnus. This latter, treated with chlorine, yields platinodiammonium chloride (Gros' chloride),  $\text{PtCl}^2.\text{N}^2\text{H}^4.\text{Cl}^2$ ; and with nitric acid the chloronitrate,  $\text{Pt}(\text{NO}^3)^2.\text{N}^2\text{H}^4.\text{Cl}^2$ .

Platosediammonium chloride forms double salts with certain metallic chlorides, especially with the chlorides of platinum. Such compounds have been obtained by Buckton and by Thomsen (1st Suppl. 953, 954). The copper salt,  $\text{PtCl}^2(\text{N}^2\text{H}^4)^2\text{CuCl}^2$ , described by Millon a. Commaille (iv. 675), may also be included in the same group.

Reiset described two salts as compounds of the chloride of this group with platinum tetrachloride, viz.:  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{Cl}^2.\text{PtCl}^4$ , and  $[\text{Pt}(\text{N}^2\text{H}^4)^2\text{Cl}^2]^2.\text{PtCl}^4$  (iv. 675); but according to Cleve these salts do not contain the tetrachloride of platinum, this compound being in fact reduced by Reiset's chloride. The first, which is red, gives, when digested with silver nitrate, chloroplatinite of silver, together with Raewsky's chlorodinitrate; it is therefore the chloroplatinite of platinodiammonium,  $\text{Pt}(\text{NH}^4)^2\text{Cl}^2.\text{PtCl}^2$ . The second is nothing but the green salt of Magnus, which is formed when the solutions used are dilute and boiling; in this case the solution contains Gros' chloride,  $\text{PtCl}^2.\text{N}^2\text{H}^4.\text{Cl}^2$ .

**Platosediammonium Bromide**,  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{Br}^2$ , obtained by decomposing the sulphate with barium bromide, crystallises in colourless flattened prisms (in cubes

according to Reiset), very soluble, and containing 3 mols.  $\text{H}_2\text{O}$ , which they lose at  $100^\circ$ . The salt is not decomposed by boiling water (Cleve).

The *iodide*,  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{I}^2$ , obtained like the bromide, crystallises in cubes. At the boiling heat it gives off  $2\text{NH}_3$ , and is converted into iodide of platossammonium.

*Nitrate*,  $\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^4(\text{NO}^3) \\ \text{N}^2\text{H}^4(\text{NO}^3) \end{smallmatrix}\right\}$ .—Obtained in colourless or yellow needles by the action of nitric acid on the chloride. It is slightly soluble in cold water; deflagrates like gunpowder. It unites directly with chlorine, bromine, and iodine, also with nitrogen tetroxide, with which it forms crystals of a fine indigo-colour. Strong nitric acid converts it into a trinitro-derivative (Cleve).

*Hydroxide*,  $\text{Pt}(\text{N}^2\text{H}^4)^2(\text{OH})^2$ .—Described in vol. iv. p. 675, as oxide.

*Sulphates*.—The *neutral sulphate*,  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{SO}^4$ , crystallises in transparent rectangular octohedrons, which, according to Poyzner, are very slightly soluble in cold water, and dissolve in 50–60 pts. of boiling water. It unites with chlorine, &c. Nitrous acid converts it into nitroplatinammonium nitrate,  $\text{N}^2\text{H}^4\text{Pt}^+(\text{NO}^2)(\text{NO}^3)$ .

The *acid sulphate*,  $(\text{N}^2\text{H}^4)^2\text{Pt}.\text{SO}^4 + 2(\text{N}^2\text{H}^4)^2\text{Pt}(\text{SO}^4\text{H})^2 + 8\text{H}_2\text{O}$ , is precipitated in nacreous scales on adding sulphuric acid to a solution of platossammonium chloride (Cleve). Another acid sulphate was accidentally obtained by Cleve in colourless, very fragile prisms containing  $2[(\text{N}^2\text{H}^4)^2.\text{Pt}.\text{SO}^4] + (\text{N}^2\text{H}^4)^2.\text{Pt}(\text{SO}^4\text{H})^2$ .

*Sulphite*.—Acid sodium sulphite forms, with platossammonium chloride, a precipitate made up of colourless needles having the composition  $3(\text{N}^2\text{H}^4)^2\text{PtSO}^3 + 2\text{PtSO}^3 + 4\text{H}_2\text{O}$ . Its solution in hydrochloric acid gives the green salt of Magnus (Cleve).

*Carbonates*.—The *neutral carbonate*,  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{CO}^3 + \text{H}_2\text{O}$ , is formed by decomposing the chloride with sodium carbonate or by exposing the hydrate to the air. On further exposure it absorbs an additional quantity of carbonic acid, and passes into the *acid carbonate*,  $\text{Pt}(\text{N}^2\text{H}^4)^2(\text{CO}^2\text{H})^2$ .

*Chromates*.—The *neutral salt*,  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{CrO}^4$ , is a lemon-yellow nearly insoluble powder (Cleve). The *dichromate*,  $\text{Pt}(\text{N}^2\text{H}^4)^2\text{Cr}_2\text{O}_7$ , is a yellow precipitate slightly soluble in water, insoluble in alcohol, crystallising from boiling water in small cubes. Its ammoniacal solution, when left to evaporate, deposits crystals of the neutral chromate. By calcination it is resolved into chromic oxide, ammonia, water, nitrogen and platinum (Buckton).

*Phosphate*,  $\text{Pt}(\text{N}^2\text{H}^4)^2.\text{PO}^4\text{H} + 2\frac{1}{2}\text{H}_2\text{O}$ .—Flattened colourless prisms, soluble in water, precipitated by alcohol. Treated with bromine it yields the *bromide*,  $\text{PtBr}^2(\text{N}^2\text{H}^4)^2.\text{Br}^2$ , and the *brominated phosphates*,  $(\text{N}^2\text{H}^4)^2(\text{PtBr}^2)\text{PO}^4$  and  $(\text{N}^2\text{H}^4)^2(\text{PtBr}^2)(\text{PO}^4\text{H})^2 + 4\text{H}_2\text{O}$ . It appears to form compounds with ammonium phosphate (Cleve).

*Organic salts*.—The *acetate*,  $(\text{N}^2\text{H}^4)^2\text{Pt}(\text{C}^2\text{H}_3\text{O}^2)^2$ , is colourless, very soluble, and crystallises in flattened prisms. The *benzoate*,  $(\text{N}^2\text{H}^4)^2\text{Pt}(\text{C}^7\text{H}_5\text{O}^2)^2$ , forms colourless scales. The *neutral tartrate*,  $(\text{N}^2\text{H}^4)^2\text{Pt}.\text{C}^4\text{H}_4\text{O}^6 + 2\text{H}_2\text{O}$ , is soluble and crystallisable. The *acid tartrate*,  $(\text{N}^2\text{H}^4)^2\text{Pt}(\text{C}^4\text{H}_4\text{O}^6)^2$ , crystallises in slender needles soluble in hot water. The *neutral oxalate* crystallises in small needles; the *acid oxalate* forms colourless soluble needles (Cleve).

### 5. **Platinammonium Compounds**, $\text{Pt}\begin{smallmatrix} \text{NH}^4\text{R} \\ \text{NH}^4\text{R} \end{smallmatrix}$ . The *chloride* of this

series, discovered by Gerhardt, is obtained by the action of chlorine on platossammonium chloride. The same chemist likewise obtained the hydrate, the nitrate, the neutral sulphate, and the basic oxalate of the series (iv. 676).

The *bromide*,  $\text{Br}^2\text{Pt}(\text{NH}^4)^2.\text{Br}^2$ , is a heavy crystalline orange-red powder, composed like the chloride, of quadratic pyramids with truncated summits.

The *iodide*,  $\text{IPt}(\text{NH}^4)^2.\text{I}^2$ , is a black non-crystalline powder obtained by digesting platossammonium iodide with tincture of iodine. With ammonia it forms a crystalline powder containing  $\text{Pt}^2(\text{NH}^4)^4\text{I}^4$ . Treated with boiling potash-solution it furnishes a yellow powder of variable composition, which gives with hydriodic acid a black amorphous powder consisting of diplatinammonium iodide,  $(\text{Pt}^2)(\text{NH}^4)^4\text{I}^4$ . This last compound, treated successively with potash and with hydriodic acid gives  $(\text{Pt}^2)(\text{NH}^4)^4\text{I}^4$ , which in its turn furnishes a still more condensed iodide  $(\text{Pt}^2)(\text{NH}^4)^4\text{I}^4$ . These iodides—whose existence, however, is not quite established—would form a homologous series,  $\text{Pt}^2(\text{NH}^4)^4\text{I}^{4+2}$ , the first term of which is the iodide of platinammonium (Cleve).

*Hydroxide*,  $(\text{OH})^2\text{Pt}(\text{NH}^4)^2(\text{OH})^2$ .—Described (iv. 676) as oxide. Obtained by treating platinammonium nitrate with excess of ammonia.

**Nitrates.**—A *basic nitrate*,  $(\text{HO})^2\text{Pt}(\text{NH}^2)^2(\text{NO}^2)^2 + 2\text{H}^2\text{O}$ , is obtained from the chloride by double decomposition. Nitric acid converts it into the *normal nitrate*,  $(\text{NO}^2)^2\text{Pt}(\text{NH}^2)^2(\text{NO}^2)^2$  (iv. 676).

**Nitrites.**—*Nitronitrite*,  $(\text{NO}^2)^2\text{Pt}(\text{NH}^2)^2(\text{NO}^2)^2$ . Obtained by the action of boiling nitric acid on platossammonium nitrite, and separated, on evaporation, in large colourless plates. With potassium iodide it yields a precipitate of platinumammonium iodide (Clove).

*Chloronitric Nitrite*,  $(\text{NO}^2)\text{ClPt}(\text{NH}^2)^2(\text{NO}^2)^2$ .—Precipitated in rhombic scales on adding hydrochloric acid to a solution of the preceding salt (Clove).

*Dichloronitrite*,  $\text{Cl}^2\text{Pt}(\text{NH}^2)^2(\text{NO}^2)^2$ .—Deposited in shining scales on adding hydrochloric acid to the boiling solution of the nitronitrite. Its solution is not precipitated by silver nitrate; but on adding silver nitrite to its hot solution, small rhombic plates are formed consisting of a double nitrite,  $(\text{NO}^2)^2\left\{\begin{smallmatrix} (\text{NH}^2)^2\text{PtCl}^2 \\ \text{Ag}^2 \end{smallmatrix}\right.$  (Clove).

The *dibromonitrite* forms microscopic rhombic plates very slightly soluble in water.

*Dichlorinated Chloronitrite*,  $\text{Cl}^2\text{Pt}\left\{\begin{smallmatrix} \text{NH}^2(\text{NO}^2) \\ \text{NH}^2\text{Cl} \end{smallmatrix}\right.$ .—Small yellow crystals deposited on adding potassium chloroplatinite to the nitronitrite.

The *sulphate*,  $\text{SO}^4\text{Pt}(\text{NH}^2)^2\text{SO}^4$ , is a yellowish mass which by solution in water is converted into the *basic sulphate*,  $(\text{OH})^2\text{Pt}(\text{NH}^2)^2\text{SO}^4 + \text{H}^2\text{O}$ , which is deposited in sparingly soluble crusts.

*Oxalates.*—The *neutral oxalate* contains  $\text{C}^2\text{O}^4\text{Pt}(\text{NH}^2)^2\text{C}^2\text{O}^4$ . The *basic oxalate*,  $(\text{OH})^2\text{Pt}(\text{NH}^2)^2\text{C}^2\text{O}^4$ , is a yellow precipitate which crystallises in laminae from boiling water and detonates by heat (Gerhardt).

#### 6. Platinosemidiammonium Compounds, $\text{R}^2\text{Pt}\left\{\begin{smallmatrix} (\text{N}^2\text{H}^2)\text{R}^* \\ \text{R} \end{smallmatrix}\right.$ .—These com-

pounds, isomeric with those of the last group, have been described by Blomstrand and y Clove (*Bull. Soc. Chim.* [2], xvii. 105).

**Chloride**,  $\text{Cl}^2\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^2\text{Cl} \\ \text{Cl} \end{smallmatrix}\right.$ .—Obtained by the action of chlorine on the chloride of platosemidiammonium (p. 994). It crystallises in six-sided rhombic leaflets, yellow and anhydrous, soluble in 300 pts. of cold water, and in 65 pts. of boiling water. At 60° it becomes olive-green. It is not decomposed by strong sulphuric acid. Potash dissolves it with evolution of ammonia. Sulphurous acid reduces it to chlorosulphite of platosemidiammonium.

The *bromide*,  $\text{Br}^2\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^2\text{Br} \\ \text{Br} \end{smallmatrix}\right.$ , is red, but in other respects resembles the chloride.

*Polyiodide*,  $\text{I}^2\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^2\text{I}^2 \\ \text{I} \end{smallmatrix}\right. = \text{Pt}(\text{N}^2\text{H}^2)\text{I}^6$ .—Obtained by the action of iodine on the chloride of platosemidiammonium (p. 994). Octohedral crystals forming a nearly black powder; soluble with purple colour.

**Nitrate**,  $(\text{OH})^2\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^2\text{NO}^2 \\ \text{OH} \end{smallmatrix}\right.$ .—On treating the chloride with silver nitrate, and adding alcohol to the filtered liquid, a precipitate is obtained which appears to have this composition. The normal nitrate has not been obtained.

**Chloronitrite**,  $\text{Cl}^2\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^2\text{NO}^2 \\ \text{NO}^2 \end{smallmatrix}\right.$ .—Long, pale-yellow, very fragile needles, obtained by the action of chlorine on the nitrite of platosemidiammonium (Blomstrand). Silver nitrate removes only half the chlorine.

The corresponding *bromonitrite* forms orange-coloured needles which react in like manner in silver salts.

A *basic chloronitrite*,  $\text{Cl}^2\text{Pt}\left\{\begin{smallmatrix} \text{N}^2\text{H}^2\text{NO}^2 \\ \text{OH} \end{smallmatrix}\right.$ , is obtained by boiling the normal chloronitrite with silver nitrite. It crystallises in pale-yellow needles.

\* The groups,  $\text{N}^2\text{H}^2 = \text{NH}^2(\text{NH}^2)$ , which figure in all these formulae, are bivalent, as in the series 3. and 4. One of their nitrogen-atoms is directly combined, on one side with the platinum, on the other with the nitrogen, of a group  $\text{NH}^2$ . For this reason the group  $\text{N}^2\text{H}^2$  must not be confounded with the group  $(\text{NH}^2)^2$ , which exists in the compounds of platossammonium and platinumammonium.

*Sulphate*,  $(\text{OH})^2\text{Pt} \begin{matrix} \nearrow \text{N}^2\text{H}^4 \\ \searrow \text{SO}^4 \end{matrix}$ .—Yellow viscous mass obtained by double decomposition.

**7. Platinomonodiammonium Compounds**,  $\text{R}^2\text{Pt} \begin{matrix} \nearrow \text{N}^2\text{H}^4\text{R} \\ \searrow \text{NH}^2\text{R} \end{matrix}$ .

*Chloride*,  $\text{Cl}^2\text{Pt} \begin{matrix} \nearrow \text{N}^2\text{H}^4\text{Cl} \\ \searrow \text{NH}^2\text{Cl} \end{matrix}$ .—Formed by the action of nitromuriatic acid on chloride of platomonodiammonium. Rhombic or hexagonal scales.

*Basic Nitrate*,  $(\text{OH})^2\text{Pt} \begin{matrix} \nearrow (\text{N}^2\text{H}^4)(\text{NO}^3) \\ \searrow (\text{NH}^2)(\text{NO}^3) \end{matrix}$  +  $\text{H}^2\text{O}$ .—Microscopic crystals deposited on concentrating the solution obtained by boiling the following salt with silver nitrate.

*Dibromonitrate*,  $\text{Br}^2\text{Pt} \begin{matrix} \nearrow (\text{N}^2\text{H}^4)(\text{NO}^3) \\ \searrow (\text{NH}^2)(\text{NO}^3) \end{matrix}$  +  $\text{H}^2\text{O}$ .—Soluble yellow crusts obtained by adding bromine to platomonodiammonium nitrate (p. 995). The *monobromonitrate* is obtained by boiling this salt with a quantity of silver nitrate just sufficient to remove half the bromine.

*Bromosulphate*,  $\text{Br}^2\text{Pt} \begin{matrix} \nearrow \text{N}^2\text{H}^4 \\ \searrow \text{NH}^2 \end{matrix} \text{SO}^4$ .—Bright-yellow crusts obtained by adding bromine to platomonodiammonium sulphate (Cleve, *Bull. Soc. Chim.* [2], xvii. 107).

**8. Platinodiammonium Compounds**,  $\text{R}^2\text{Pt} \begin{matrix} \nearrow \text{NH}^2(\text{NH}^4)\text{R} \\ \searrow \text{NH}^2(\text{NH}^4)\text{R} \end{matrix}$  or

$\text{R}^2\text{Pt} \begin{matrix} \nearrow (\text{N}^2\text{H}^4)\text{R} \\ \searrow (\text{N}^2\text{H}^4)\text{R} \end{matrix}$ . Several of these compounds were discovered by Gros and by

Raewsky (iv. 675) and numerous others have been obtained by Cleve. They are formed by addition of an electronegative element to the platomonodiammonium compounds, or by the oxidation of the latter. One half of the electro-negative element or radicle contained in these compounds—that half, namely, which is directly united to the platinum—is difficult to remove, or cannot be removed at all by double decomposition; such, for example, is the case with the chlorine in Gros' salts, which can only be partially replaced by the action of silver salts.

*Chloride*,  $\text{Cl}^2\text{Pt} \begin{matrix} \nearrow \text{N}^2\text{H}^4\text{Cl} \\ \searrow \text{N}^2\text{H}^4\text{Cl} \end{matrix}$ .—This is Gros' chloride (iv. 676), obtained by treating the corresponding nitrate with hydrochloric acid, or by passing chlorine into a solution of platomonodiammonium chloride.

A *basic chloride*,  $(\text{OH})\text{ClPt}(\text{N}^2\text{H}^4)^2\text{Cl}^2$ , is obtained in microscopic insoluble needles by adding sal-ammoniac to a solution of the basic monochloronitrate.

*Raewsky's Chloride*,  $\text{PtCl}^2\text{O}(\text{N}^2\text{H}^4)^2\text{Cl}^2$  (?).—Obtained by decomposing the basic chloronitrate,  $\text{Pt}^2(\text{Cl}^2\text{O})(\text{N}^2\text{H}^4)^2\text{O}^2(\text{NO}^3)^2$  (iv. 677), with excess of hydrochloric acid. It is moderately soluble in cold and much more soluble in boiling water; less soluble in hydrochloric acid, which renders its aqueous solution turbid.

The *chloroplatinite* and *chloroplatinate* are formed by adding sodium chloroplatinite or chloroplatinate to platinodiammonium dichloronitrate.

*Bromide*,  $\text{Br}^2\text{Pt}(\text{N}^2\text{H}^4)^2\text{Br}^2$ .—Slightly soluble microscopic needles precipitated or adding a soluble bromide to the nitrate of dibromoplatinodiammonium. When boiled with solution of silver nitrate it yields silver bromide, and a solution which on cooling deposits yellow, slightly soluble crystals, probably a basic bromonitrate (Cleve).

The *basic bromide*,  $(\text{OH})\text{BrPt}(\text{N}^2\text{H}^4)\text{Br}^2$ , obtained like the basic chloride, is a pale yellow crystalline precipitate.

*Iodide*,  $\text{I}^2\text{Pt}(\text{N}^2\text{H}^4)^2\text{I}^2$ .—Graphitoidal powder converted by ammonia into yellow crystalline powder containing  $\text{Pt}(\text{NH}^2)^2(\text{NH}^4)^2\text{I}^2$  +  $\text{H}^2\text{O}$ , or more probably  $\text{I}^2(\text{Pt})^2 \begin{matrix} \nearrow (\text{N}^2\text{H}^4)^2\text{I}^2 \\ \searrow (\text{N}^2\text{H}^4)^2\text{O}^2 \end{matrix}$ .

*Chlorobromide*,  $\text{BrClPt}(\text{N}^2\text{H}^4)^2\text{BrCl}$ .—Raewsky obtained this salt by treat-

platosediammonium chloride with bromine (iv. 676). It may also be formed by double decomposition, either between ammonium chloride and platinodiammonium dibromonitrate, or between ammonium bromide and platinodiammonium dichloronitrate. It is a yellow precipitate which, when treated with hydrochloric acid, exchanges part of its bromine for chlorine, and gives with silver nitrate a mixture of silver chloride and bromide, and of the two salts,  $(\text{OH})\text{BrPt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$  and  $(\text{OH})\text{ClPt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ . A compound containing 1 at. bromine to 3 at. chlorine is obtained by precipitating the basic bromonitrate with hydrochloric acid (Cleve).

The *chloriodides*, formed under similar conditions, do not appear to be of constant composition. One containing  $(\text{ClPt})\text{Pt}(\text{N}^2\text{H}^2)^2\text{Cl}^2$  is obtained in small brown octahedrons by the action of hydriodic acid on the iodonitrate of diplatinotetradiammonium (Cleve).

The *basic chlorobromides*,  $(\text{OH.Cl})\text{Pt}(\text{N}^2\text{H}^2)^2\text{Br}^2$  and  $(\text{OH.Br})\text{Pt}(\text{N}^2\text{H}^2)^2\text{Cl}^2$ , are crystalline precipitates (Cleve).

*Ferrocyanide*.—Gros' nitrate,  $\text{Cl}^2\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ , treated with solution of potassium ferrocyanide, yields a violet precipitate, which appears to have the composition,  $(\text{FeCy}^2\text{K})[\text{PtO}(\text{N}^2\text{H}^2)^2\text{Cy}^2]^2$ . The mother-liquors yield the platosediammonium cyanide analogous to the green salt of Magnus.

The *chlorosulphocyanate*,  $\text{Cl}^2\text{Pt}(\text{N}^2\text{H}^2)^2(\text{CNS})^2$ , is an orange-coloured crystalline precipitate.

*Nitrates*.—The *normal nitrate*,  $(\text{NO}^2)^2\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ , is not known.

The *basic nitrate*,  $(\text{OH.NO}^2)\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$  (Gerhardt's oxy-nitrate, iv. 677), is formed by the action of nitric acid on platosediammonium nitrate; also by the action of silver nitrate on the iodonitrate. It is a white very soluble crystalline powder. Treated with ammonia it yields the bibasic nitrate,  $(\text{OH})^2\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ , which forms a white amorphous powder detouring when heated and turned blue by sulphuric acid. Hydrochloric acid converts it into Gros' chloride.

*Dinitronitrate*,  $(\text{NO}^2)^2\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ .—This salt is formed under various circumstances, especially by the action of nitrous vapours on platosediammonium sulphate. It is precipitated in small well-defined octahedrons of an indigo-blue colour, which decompose when dissolved in water, giving off nitrous vapours.

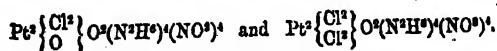
*Chloronitrates: a.*  $(\text{Cl.NO}^2)\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ .—White crystalline precipitate formed on adding nitric acid to the solution of the following salt. Decomposed by water into acid and the basic salt *b*.

*b.*  $(\text{OH.Cl})\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ .—White microscopic slightly soluble crystals, obtained by the action of silver nitrate on the salt *c*. Prolonged boiling with silver nitrate is required to remove the chlorine. Cleve, who prepared this salt, regards it as identical with one of Raewsky's nitrates (iv. 677).

*c.*  $\text{ClPt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$  (Gros' nitrate, iv. 677).—Obtained by boiling the green salt of Magnus with strong nitric acid; also by the action of chlorine on nitrate of platosediammonium.

*d.*  $(\text{NO}^2)^2\text{Pt}(\text{N}^2\text{H}^2)^2\text{Cl}^2$ .—This salt, isomeric with the preceding, is distinguished from it by the fact that its chlorine is easily precipitated by silver nitrate, whereas the group  $(\text{NO}^2)^2$ , which is united with the platinum, is not removed by double decomposition; Gros' nitrate, on the contrary, gives scarcely any precipitate with silver nitrate, even after a long time. The salt *d* is obtained by the action of hydrochloric acid on a boiling solution of the basic nitrate of platinodiammonium. It is then deposited as a white powder made up of small right prisms; when recrystallised by slow evaporation it forms large crystals containing  $\text{H}^2\text{O}$ . With platinic chloride it forms an orange-red double salt containing  $(\text{NO}^2)^2\text{Pt}(\text{N}^2\text{H}^2)^2\text{Cl}^2 + \text{PtCl}^4 + 2\text{H}^2\text{O}$  (Cleve).

*Raewsky's Nitrates*.—By boiling the green salt of Magnus with a large excess of nitric acid, Raewsky obtained two salts whose composition he represented by the formulæ:



The first, which is but slightly soluble in nitric acid, separates in small shining crystals, and the second crystallises with difficulty from the mother-liquor. These salts form the points of departure of two series, a few members of which were obtained by Raewsky. Their constitution, supposing the analyses to be correct, is very difficult to determine. Gerhardt supposed them each to contain 2 at. oxygen less, and regarded them as sesqui-acid salts of diplatinamine (iv. 677). They probably belong to the diplatinodiammonium group.

*Bromonitrates* (Cleve, loc. cit.)—*a.*  $(\text{Br.NO}^2)\text{Pt}(\text{N}^2\text{H}^2)^2(\text{NO}^2)^2$ . Orange-coloured

crystalline powder, decomposable by water, obtained by the action of nitric acid on the boiling solution of the following salt.

b.  $(\text{Br} \cdot \text{OH})\text{Pt}(\text{N}^2\text{H}^4)(\text{NO})^2$ . Pale yellow, slightly soluble granular salt, obtained by the action of silver nitrate on the salt c.

c.  $\text{Br}^2\text{Pt}(\text{N}^2\text{H}^4)(\text{NO})^2$  (*Brominated salt of Gros*). Prepared like the corresponding chloronitrate. Crystallises in lemon-yellow soluble flattened prisms. When boiled with silver nitrate it gives up half of its bromine and is converted into the salt b.

\* *Iodonitrate*,  $\text{IPt}(\text{N}^2\text{H}^4)(\text{NO})^2$ .—Prepared by the action of iodine on platino-ammonium nitrate. Nearly black crystals of the same form as the chloronitrate. Silver nitrate at the boiling heat removes half the iodine, forming the basic iodonitrate. Ammonia precipitates from its solution a dingy yellow powder formed of microscopic needles, and constituting perhaps, according to Cleve, the oxyiodonitrate of diplatinetetradiammonium.

*Nitro-iodonitrate*,  $(\text{NO})_2\text{IPt}(\text{N}^2\text{H}^4)(\text{NO})^2$ .—Orange-brown crystals obtained by the action of nitric acid on the oxy-iodide of diplatinetetradiammonium (Cleve).

*Carbonates*.—a.  $[(\text{NO})_2\text{Pt}(\text{N}^2\text{H}^4)]^2(\text{CO}_3)^2$  (?). White crystalline powder obtained by adding ammonia sesquicarbonate to the basic nitrate.

b.  $[\text{BrPt}(\text{N}^2\text{H}^4)]^2(\text{CO}_3)^2 + 4\text{H}_2\text{O}$ . Yellow crystalline powder obtained in the same way as the dibromonitrate. It unites with the dibromonitrate, forming a double salt which crystallises in yellow microscopic prisms.

c. A compound of the monochlorocarbonate with Gros' chloronitrate is obtained by pouring a solution of the latter into a boiling solution of ammonium carbonate.

d.  $(\text{OH} \cdot \text{Cl})\text{Pt}(\text{N}^2\text{H}^4)\text{CO}_2$ . Formed by adding Gros' nitrate to excess of sodium carbonate (Cleve).

e. *Raewsky's Carbonate*,  $(\text{O} \cdot \text{Cl})^2\text{Pt}^2(\text{N}^2\text{H}^4)_2\text{O}_2(\text{CO}_3)^2$ .—White granular, very soluble precipitate (iv. 678).

*Sulphates*.—The *neutral sulphate*,  $(\text{SO}_4\text{Pt})(\text{N}^2\text{H}^4)_2\text{SO}_4 + 2\text{H}_2\text{O}$ , is a white amorphous powder formed by the action of sulphuric acid on the basic nitrate.

A *basic sulphate*,  $\text{SO}_4\left\{\begin{array}{l} \text{Pt}(\text{OH})\text{N}^2\text{H}^4 \cdot \text{N}^2\text{H}^4 \cdot \text{SO}_4 \\ \text{Pt}(\text{OH})\text{N}^2\text{H}^4 \cdot \text{N}^2\text{H}^4 \cdot \text{SO}_4 \end{array}\right. + 3\text{H}_2\text{O}$ , is obtained by precipitating a hot solution of the neutral bromonitrate with silver sulphate, and evaporating the filtrate. Colourless flattened prisms, soluble in water. Barium chloride throws down from its solution only a third of the sulphuric acid, showing that part of this acid is contained in the radicle (Cleve). This salt yields, by double decomposition, a series of salts, the *hydroxyl-sulphoplatodiammonium salts*, containing non-precipitable sulphuric acid (*infra*).

Another basic sulphate is formed, according to E. Davy, on boiling a solution of platonic sulphate neutralised with ammonia. It is precipitated as a light brown powder, slightly explosive, insoluble in water, soluble in acids.

*Chlorosulphate*,  $\text{ClPt}(\text{N}^2\text{H}^4)_2\text{SO}_4$  (see iv. 677).

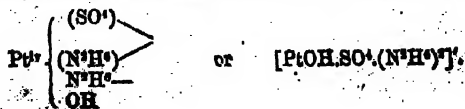
*Monochloro-trisulphate*,  $\text{PtCl}\left\{\begin{array}{l} \text{SO}_4 \\ \text{PtCl} \end{array}\right\}\left\{\begin{array}{l} (\text{N}^2\text{H}^4)_2\text{SO}_4 \\ (\text{N}^2\text{H}^4)_2\text{SO}_4 \end{array}\right.$ .—Delicate prisms obtained by treating Gros' chlorocarbonate with sulphuric acid (Cleve).

*Bromosulphate*,  $\text{BrPt}(\text{N}^2\text{H}^4)_2\text{SO}_4$ .—Lemon-yellow, very soluble, crystalline powder. Its solution, mixed with a quantity of silver nitrate sufficient to precipitate only half the bromine, yields a solution which deposits yellow needles having the composition  $\text{PtBr}\left\{\begin{array}{l} (\text{N}^2\text{H}^4)_2\text{SO}_4 \\ \text{PtBr} \end{array}\right\}\left\{\begin{array}{l} (\text{N}^2\text{H}^4)_2\text{SO}_4 \\ (\text{N}^2\text{H}^4)_2\text{SO}_4 \end{array}\right.$ . From this salt barium chloride throws down two-thirds of the sulphuric acid.

*Iodosulphate*,  $\text{IPt}(\text{N}^2\text{H}^4)_2\text{SO}_4$ .—Brown crystalline powder slightly soluble in water.

*Chloronitric and Bromonitric Sulphates*.—These salts are obtained in the crystalline state by dissolving the monochloro- or monobromo-nitrate in sulphuric acid, and pouring the solution into water. The former,  $(\text{Cl} \cdot \text{NO})\text{Pt}(\text{N}^2\text{H}^4)_2\text{SO}_4 + \text{H}_2\text{O}$ , is white; the latter, which contains Br in place of Cl, is yellow (Cleve).

**HYDROXYLSULPHOPLATODIAMMONIUM COMPOUNDS** (Cleve, *Bull. Soc. Chim.* [2], xv. 162). These compounds are derived from the basic sulphate,  $\text{SO}_4[\text{Pt}(\text{OH})(\text{N}^2\text{H}^4)\text{SO}_4]^2 + 3\text{H}_2\text{O}$ , above described, which contains the group  $\text{SO}_4$  in direct combination with platinum, and not removable by double decomposition with barium salts. They may be supposed to contain the univalent radicle:





**Chloride**,  $[\text{PtOH.SO}^4(\text{N}^2\text{H}^5)^2]\text{Cl} + 2\text{H}^2\text{O}$ .—Obtained by decomposing the basic sulphate above mentioned with barium chloride. Forms colourless truncated prisms soluble in water. The solution mixed with hydrochloric acid deposits the salt in the anhydrous state. The chlorine of this salt is precipitated by silver nitrate, but the sulphuric acid is not precipitated by barium chloride.

The corresponding *chloroplatinate* forms orange-coloured flattened crystals, containing  $2\text{H}^2\text{O}$ .

**Bromide**.—Obtained like the chloride, and likewise contains  $2\text{H}^2\text{O}$ . Flattened crystals, colourless or yellowish.

**Nitrate**,  $[\text{PtOH.SO}^4(\text{N}^2\text{H}^5)^2]\text{NO}^3$ .—White crystalline, slightly soluble powder.

**Sulphate**.—Already described (p. 1000).

**Chromates**.—The *neutral salt*,  $[\text{PtOH.SO}^4(\text{N}^2\text{H}^5)^2]^2\text{CrO}^4 + 2\text{H}^2\text{O}$ , obtained like the chloride, forms rounded groups of yellow crystals. The *dichromate* is an orange-coloured, sparingly soluble precipitate.

**Oxalate**,  $[\text{PtOH.SO}^4(\text{N}^2\text{H}^5)^2]^2\text{C}^2\text{O}^4 + 2\text{H}^2\text{O}$ .—Crystalline precipitate.

On attempting to prepare the corresponding *hydroxide*,  $[\text{PtOH.SO}^4(\text{N}^2\text{H}^5)^2]\text{OH}$ , by the action of baryta on the sulphate, a colourless alkaline solution was obtained, which, on evaporation, suddenly yielded colourless sparingly soluble crystals, consisting of an isomeric form of this hydroxide, viz.: the *basic sulphate*,  $\text{SO}^4\text{Pt}(\text{OH})^2(\text{N}^2\text{H}^5)^2$ .

**Platinodiammonium Chromates**.—Cleve has examined the following chromates, all of which form yellow or orange-coloured crystallisable precipitates. They are obtained by double decomposition:



**Platinodiammonium Phosphates**.—Gros, by adding an alkaline phosphate to the dichloronitrate of this series, obtained small shining transparent crystals, very slightly soluble in water. Cleve has obtained the following salts:

- a.  $\text{Pt}(\text{NO}^3)(\text{N}^2\text{H}^5)^2.\text{PO}^4 + \text{H}^2\text{O}$
- b.  $\text{PtCl}^2(\text{N}^2\text{H}^5)^2.\text{PO}^4 + 2\text{H}^2\text{O}$
- c.  $\text{PtBr}^2(\text{N}^2\text{H}^5)^2.\text{PO}^4 + 2\text{H}^2\text{O}$
- d.  $\text{PtBr}^2(\text{N}^2\text{H}^5)^2(\text{PO}^4\text{H}^2)^2 + 2\text{H}^2\text{O}$
- e.  $[\text{Pt}(\text{NO}^3)(\text{OH})(\text{N}^2\text{H}^5)^2]^2\text{C}^2\text{O}^4 + \text{H}^2\text{O}$ .

The salts *a* and *c* are obtained by adding disodic phosphate, or the pyrophosphate, to the basic nitrate of platinodiammonium; *b* and *c* in like manner from the chloro- or bromo-nitrate of Gros. They are crystalline and slightly soluble. Lastly *d* is obtained by adding bromine to the phosphate of platodiammonium; it is moderately soluble and crystallises in lemon-yellow flattened prisms.

**Racwsky's Phosphate**,  $\text{Pt}^2(\text{Cl}^2\text{O})(\text{N}^2\text{H}^5)^4\text{O}^2(\text{PO}^4\text{H}^2)^2$ , separates in crystalline tufts on mixing hot strong solutions of the corresponding chloronitrate and trisodic phosphate (iv. 677).

**Platinodiammonium Oxalates** (iv. 677, 678).—Gros' *oxalate*,  $\text{PtCl}^2(\text{N}^2\text{H}^5)^2\text{C}^2\text{O}^4$ , is a white, crystalline, very soluble powder, obtained by double decomposition with Gros' nitrate and ammonium oxalate. The corresponding brominated salt is yellow.

**Racwsky's Oxalate**,  $\text{Pt}^2(\text{Cl}^2\text{O})(\text{N}^2\text{H}^5)^4\text{O}^2(\text{C}^2\text{O}^4)^2$ , is a white crystalline precipitate nearly insoluble in boiling water.

The *mononitric oxalate*,  $\text{Pt}(\text{OH.NO}^3)(\text{N}^2\text{H}^5)^2\text{C}^2\text{O}^4$ , is obtained in white flocks on adding ammonium oxalate to basic nitrate of platinodiammonium. It detonates when heated (Gerhardt).

**ACETHYDROXYL-PLATINODIAMMONIUM COMPOUNDS** (Cleve).—Bromo-sulphate of platinodiammonium, decomposed by basic lead acetate, yields a *basic aceto-sulphate*—



in which the group  $\text{SO}^4$  may be replaced by double decomposition. It may accordingly be supposed to contain the radicle  $[\text{Pt}(\text{OH.C}^2\text{H}^3\text{O}^2)(\text{N}^2\text{H}^5)^2]^2$ , which for shortness may be represented by the symbol R.

**Chloride**,  $2\text{ROCl}^2 + \text{H}^2\text{O}$ .—Small, colourless, moderately soluble needles. Silver nitrate removes the whole of the chlorine. The *chloroplatinate*,  $\text{PtCl}^2\text{R} + 2\text{H}^2\text{O}$ , crystallises in orange-red, moderately soluble needles.

**Nitrate**,  $R(NO^3)^2 + H^2O$ .—White crystalline powder, slightly soluble in cold water.

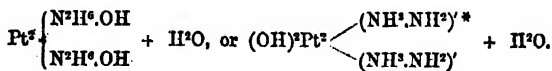
**Sulphate**,  $2(SO^4.R) + 3H^2O$ .—This salt, whose formation is given above, is deposited on evaporation in rather large, well-defined, colourless crystals.

**Dichromate**,  $Cr_2O^7.R + H^2O$ .—Orange-coloured precipitate, which gives off its water at  $100^\circ$ .

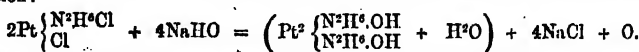
9. **Diplatinaammonium**,  $=(Pt^2)^2(NH^3)^4$ .—The only known compound of this radicle is the iodide  $I^2Pt^2(NH^3)^4I^2$ , which is a crystalline powder obtained by the action of ammonia on the iodide of platinammonium,  $I^2Pt(NH^3)^2I^2$  (p. 996).

10. **Diplatensodiammonium**,  $=(Pt^2)^2(N^2H^3)^2$ , or  $=(Pt^2)^2 \begin{matrix} (NH^2NH^3) \\ (NH^2NH^3) \end{matrix}$  (Cleve,

*Bull. Soc. Chim.* [2], xvii. 100).—When the chloride of platosemidiammonium is boiled with soda, a greyish, pseudomorphic, crystalline, insoluble powder is obtained, which detonates violently when heated. This powder, which forms black compounds with acids, constitutes the hydroxide of diplatensodiammonium or of diplatinosomidiammonium:



The first of these formulæ was proposed by Blomstrand, the second by Cleve, who discovered this base and its salts. The difference of  $H^2$  between the two formulæ is too small to be detected by analysis. Cleve bases his opinion on the formation of this hydroxide, which, if Blomstrand's view were correct, should take place according to the equation:



Conversely, the action of hydrochloric acid on the hydroxide, which ultimately produces the chloride of platosemidiammonium, ought to be attended with disengagement of hydrogen. Cleve, however, has never observed either oxidation or disengagement of oxygen in the first case, or disengagement of hydrogen in the second. Nitromuriatic acid transforms the hydroxide into diplatiniodiammonium chloride,  $(Pt^2)^2(N^2H^3)^2Cl^4$ .

**Diplatinosomidiammonium Chloride**,  $Cl^2Pt^2(NH^2.NH^3)^2$ .—The hydroxide just described is converted by hydrochloric acid into a yellow powder which boiling water converts into a black powder, while chloride of platinosomidiammonium passes into solution. The black substance is the chloride of platinosomidiammonium.

**Nitrate**,  $(NO^3)^2Pt^2(NH^2.NH^3)^2$ .—Black, amorphous, insoluble powder, which detonates violently when heated.

**Sulphate**,  $SO^4.Pt^2(NH^2.NH^3)^2$ .—Black insoluble powder.

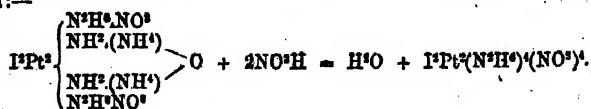
11. **Diplatiniodiammonium Compounds**,  $R^2(Pt^2)^2 \begin{Bmatrix} NH^3(NH^2) \\ NH^3(NH^2) \end{Bmatrix}$  The only

compound of this series yet obtained is the *chloride*,  $Cl^2Pt^2(NH^2.NH^3)^2 + H^2O$ , which is a yellow amorphous powder formed by the action of nitromuriatic acid on the hydroxide of the preceding series (Cleve).

12. **Diplatino-tetradiammonium Compounds**,  $R^2(Pt^2)^2(N^2H^3)^4R^4$  (Cleve, *Bull. Soc. Chim.* [2], xv. 168). Racwsky's salts (iv. 677) may be included in this series.

**Iodide**,  $I^2Pt^2(N^2H^3)^4I^2$ .—Black powder obtained by adding potassium iodide to the iodonitrate.

**Nitrates**: **Iodonitrate**,  $I^2Pt^2(N^2H^3)^4(NO^3)^4$ .—Produced by the action of nitric acid on the oxydo-nitrate of diplatino-tetradiammonium (*infra*), according to the equation:—



It is an orange-coloured powder which dissolves in hot water and crystallises in small prisms. It contains 8 or 4 mols. of water which it gives off at  $100^\circ$ . Its solution is not precipitated by silver nitrate in the cold, but on heating the liquid, silver iodide is

\* The formula  $NH^2.NH^3$  is that of ammonium in which 1 at. of hydrogen is replaced by amidogen.

slowly deposited. With ammonia it gives a precipitate of the oxyiodonitrate. Hydrochloric acid converts it into a brown crystalline powder consisting of chloriodoplatinodiammonium chloride,  $\text{Pt}(\text{ClI})(\text{N}^2\text{H}^4)^2\text{Cl}^2$ . Bromine decomposes the iodonitrate, liberating the iodine and forming several products, and amongst others, yellow microscopic prisms having the composition  $(\text{PtI})^2(\text{NH}^2)^2(\text{NO}^2)\text{Br}^2$ .

The iodonitrate yields, by double decomposition, the three following salts:—

*Iodosulphate*,  $\text{I}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{SO}^4)^2$ .—Yellow, amorphous, insoluble powder.

*Iodophosphate*,  $\text{I}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{PO}^4\text{H})^2$ .—Yellow precipitate, formed of microscopic needles.

*Iodoxalate*,  $\text{I}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{C}^2\text{O}^4)^2$ .—Bulky yellow powder.

*Basic Nitrate*,  $(\text{HO})^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{NO}^2)^4$ .—Formed by boiling the oxyiodonitrate with silver nitrate, and deposited gradually from the colourless solution as a white crystalline powder, very slightly in cold water, detonating violently when heated. It contains 2 mols.  $\text{H}_2\text{O}$ , which it gives off at  $100^\circ$ .

The *neutral nitrate*,  $(\text{NO})^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{NO}^2)^4 + 4\text{H}_2\text{O}$ , is formed by adding nitric acid to the basic nitrate. Resolved by water into nitric acid and the basic nitrate.

The *basic nitrate* yields by double decomposition the following salts:—

*Chloride*,  $(\text{OH})^2(\text{Pt}^2)(\text{N}^2\text{H}^4)\text{Cl}^4 + \text{H}_2\text{O}$ .—White microscopic needles very slightly soluble, completely decomposed by silver nitrate.

*Sulphate*,  $(\text{OH})^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{SO}^4)^2 + 2\text{H}_2\text{O}$ .—White amorphous powder.

*Orthophosphate*,  $(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{PO}^4)^2 + 2\text{H}_2\text{O}$ .—Bulky white powder.

*Dichromate*,  $(\text{OH})^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{Cr}^2\text{O}^7)^2$ .—Orange-coloured precipitate.

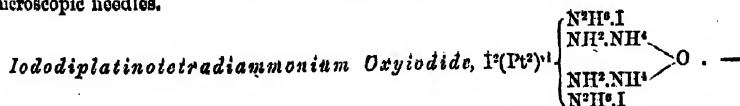
*Oxalate*,  $(\text{HO})^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{C}^2\text{O}^4)^2 + 2\text{H}_2\text{O}$ .—White precipitate.

*Bromonitrate*,  $\text{Br}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{NO}^2)^4 + 2\text{H}_2\text{O}$ .—Formed by adding bromine to the basic nitrate. Small yellow crystals moderately soluble in hot water. The solution does not precipitate silver nitrate. Ammonia throws down from it a yellow crystalline powder consisting of a bromodinirate. The bromonitrate yields by double decomposition the three following salts:—

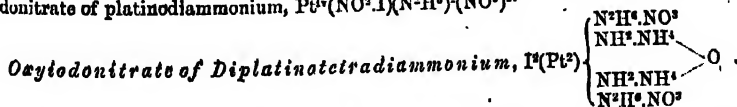
*Bromochloride*,  $\text{Br}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)\text{Cl}^4$ .—Yellowish-white precipitate, formed of microscopic needles.

*Bromosulphate*,  $\text{Br}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)(\text{SO}^4)^2 + 2\text{H}_2\text{O}$ .—Yellowish-white precipitate, giving off its water at  $100^\circ$ .

*Acid Bromoxalate*,  $\text{Br}^2(\text{Pt}^2)(\text{N}^2\text{H}^4)\left\{\begin{smallmatrix} \text{C}^2\text{O}^4 \\ (\text{C}^2\text{O}^4\text{H})^2 \end{smallmatrix}\right\}$ .—White precipitate composed of microscopic needles.



This is the yellow powder formed by the action of ammonia on platinumammonium iodide (p. 998). Nitric acid attacks it, giving off vapours of iodine, and forming the nitroiodonitrate of platinodiammonium,  $\text{Pt}^2(\text{NO}^2\text{I})(\text{N}^2\text{H}^4)(\text{NO}^2)^2$ .



—Yellow microscopic needles obtained by the action of ammonia on the iodonitrate of platinodiammonium (p. 1000). Nitric acid converts it into the iodonitrate of diplatinotetradiammonium above described.

To these oxidised compounds probably belong Rasowsky's salts (iv. 677, 678), although they are said to contain 2 or 3 atoms of oxygen, which is doubtful.

#### Ammoniacal Platinum-Compounds containing Organic Radicles.

The methylamine and ethylamine salts,  $\text{PtCl}^4(\text{CH}_3\text{N})^4$ ,  $\text{PtCl}^4$  and  $\text{PtCl}^4(\text{C}^2\text{H}_5\text{N})^4$ ,  $\text{PtCl}^4$ , analogous to the green salt of Magnus, were discovered in 1850 by Wurtz (iv. 679), who likewise obtained the corresponding chlorides and sulphates. Other ethylamine platinum-compounds have been obtained by Gordon (*Deut. Chem. Ges. Ber.* iii. 174) and by Cleve (*Bull. Soc. Chim.* [2], xvii. 294), who has also studied especially the ammoniacal platinum-compounds containing phenyl.

1. **Platosomethylammonium.** The chloride of this base,  $\text{Pt}(\text{CH}_3\text{N})^2\text{Cl}^2$ , appears to be obtained by heating the chloride of platosodimethylammonium and dissolving the residue in boiling water (Wurtz).

2. **Platosodimethylammonium.** The *chloroplatinite* of this base,  $\text{Pt}[\text{N}^2(\text{CH}_3)^2\text{H}^4]^2\text{Cl}^2 \cdot \text{PtCl}_2$ , analogous to the green salt of Magnus, is formed by the action of a strong solution of ethylamine on platinous chloride, the mixture becoming hot and the chloroplatinite being deposited in the form of a chrome-green powder. On treating it with excess of methylamine in sealed tubes heated in the water-bath, it gives the *chloride*,  $\text{Pt}[\text{N}^2(\text{CH}_3)^2\text{H}^4]^2\text{Cl}^2$ , which solidifies to a crystalline mass when its solution is evaporated to a syrup. This chloride is less soluble in alcohol than in water. On heating it to  $160^\circ$  and treating the residue with boiling water, a solution is obtained which deposits small shining crystals, probably consisting of the chloride of platosomethylammonium. The green methylic salt treated with nitric acid yields crystals of a nitrate,  $(\text{NO}_3)^2[\text{N}^2(\text{CH}_3)^2\text{H}^4]^2 \cdot \text{PtCl}_2$ , analogous to Gros' nitrate (p. 990) (Wurtz).

3. **Platosethylammonium,**  $\text{Pt} \begin{cases} \text{N}(\text{C}^2\text{H}_5)\text{H}^2- \\ \text{N}(\text{C}^2\text{H}_5)^2\text{H}^2- \end{cases}$ . Only one compound of this base is known, viz., the *iodide*, the formation of which will be mentioned further on.

4. **Platosodiethylammoniums,**  $\text{Pt} \begin{cases} \text{N}^2\text{H}^4- \\ \text{N}^2(\text{C}^2\text{H}_5)^2\text{H}^4- \end{cases}$ ;  $\text{Pt} \begin{cases} \text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)\text{H}^2 \\ \text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)^2\text{H}^2 \end{cases}$   
and  $\text{Pt} \begin{cases} \text{N}^2(\text{C}^2\text{H}_5)^2\text{H}^4- \\ \text{N}^2(\text{C}^2\text{H}_5)^2\text{H}^4- \end{cases}$ .

The *chloride* of the first of these bases,  $\text{Pt} \begin{cases} \text{N}^2\text{H}^4\text{Cl} \\ \text{N}^2(\text{C}^2\text{H}_5)\text{H}^4\text{Cl} \end{cases}$ , is formed by boiling platosamidiammonium chloride (p. 904) with aqueous ethylamine (Cleve); also by the action of ammonia on the ethylated green salt of Magnus (Gordon). It is not produced by the action of ethylamine on the ordinary green salt. It is a very soluble crystalline mass, the solution of which forms, with platinous chloride, a compound analogous to the green salt of Magnus (Cleve).

Its isomeride, the chloride,  $\text{Pt} \begin{cases} \text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)\text{H}^2\text{Cl} \\ \text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)^2\text{H}^2\text{Cl} \end{cases}$ , is formed by the action of ethylamine on platosammonium chloride. It is much less soluble than the preceding modification, and crystallises in beautiful white needles. Its solution forms, with potassium iodide, white nacreous scales,  $\text{Pt}[\text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)\text{H}^2]^2\text{I}^2$ , which, when boiled, give off ammonia, and are converted into a yellow crystalline powder.

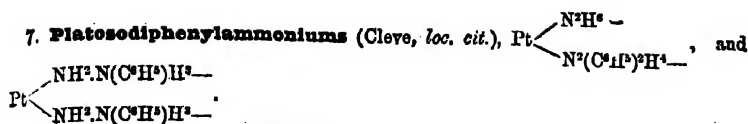
The *chloroplatinite*,  $\text{Pt}[\text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)\text{H}^2]^2\text{Cl}^2 \cdot \text{PtCl}_2$ , forms green shining sparingly soluble needles. The *sulphate*,  $\text{Pt}[\text{NH}^2 \cdot \text{N}(\text{C}^2\text{H}_5)\text{H}^2]^2 \cdot \text{SO}_4^2 + 6\text{H}_2\text{O}$ , is very soluble, and crystallises in fine colourless prisms which give off their water at  $100^\circ$  (Cleve).

The *chloroplatinite* of the tetraethylated base,  $\text{Pt}(\text{NH}^2\text{C}^2\text{H}_5)^4\text{Cl}^2 \cdot \text{PtCl}_2$ , or  $(\text{C}^2\text{H}_5\text{N})^2\text{PtCl}_2$ , is the chamois-coloured salt which Wurtz obtained by the action of ethylamine on platinous chloride (iv. 679).

5. **Platosodibutylammonium.** The *chloroplatinite*, analogous to the green salt of Magnus, is a green powder formed by the action of butylamine on platinous chloride. Treated with excess of butylamine, it yields the *chloride*  $\text{Pt}[\text{N}^2(\text{C}^4\text{H}_9)^2\text{H}^4]^2\text{Cl}^2$ , and with ammonia it yields the *chloride* of *platomonobutylidiammonium*,  $\text{Pt}[\text{NH}^2 \cdot \text{N}(\text{C}^4\text{H}_9)\text{H}^2]^2\text{Cl}^2$  (Gordon).

6. **Platosophenylammonium,**  $\text{Pt} \begin{cases} \text{N}(\text{C}^6\text{H}_5)\text{H}^2- \\ \text{N}(\text{C}^6\text{H}_5)^2\text{H}^2- \end{cases}$ . The *chloroplatinite*,  $\text{PtCl}_2 \cdot \text{N}^2(\text{C}^6\text{H}_5)^2\text{H}^4 \cdot \text{PtCl}_2$ , analogous to the green salt of Magnus, is easily formed by the action of aniline on platinous chloride, but is not altered by aniline; it dissolves in water when boiled, and crystallises therefrom in yellow needles which are insoluble in water, alcohol, and ether, and are not altered by hydrochloric or dilute nitric acid (Gordon).

The corresponding *tbluidine salt*,  $\text{PtCl}_2 \cdot \text{N}^2(\text{C}^6\text{H}_7)\text{H}^4 \cdot \text{PtCl}_2$ , is a yellowish powder similar in its properties to the aniline salt. The *xylydine salt*,  $\text{PtCl}_2 \cdot \text{N}^2(\text{C}^6\text{H}_7)\text{H}^4 \cdot \text{PtCl}_2$ , forms whitish needles (Gordon).



a. The *chloride*,  $\text{Pt} \begin{cases} \text{N}^2\text{H}^+.\text{Cl}^- \\ \text{N}^2(\text{C}^6\text{H}_5)_2\text{H}^+.\text{Cl}^- \end{cases}$ , obtained by heating platosamidiammonium chloride in a sealed tube with excess of aniline mixed with dilute alcohol, is a white crystalline powder which may be freed from coloured products by washing with alcohol. With potassium chloroplatinite it forms a bulky precipitate,  $\text{PtCl}_2[\text{N}^2\text{H}^+.\text{N}^2(\text{C}^6\text{H}_5)_2\text{H}^+].\text{PtCl}_2$ , analogous to the green salt of Magnus.

Cleve thinks it probable that there exists also a chloride having the composition  $\text{Pt} \left\{ \begin{smallmatrix} (\text{NH}^2)^2 \\ (\text{C}^6\text{H}_5\text{N})^2 \end{smallmatrix} \right\} \text{Cl}_2$ , as he once obtained a chloride intermediate in composition between this and the one above described.

The *nitrate*,  $\text{Pt} \begin{cases} \text{N}^2\text{H}^+.\text{NO}_3^- \\ \text{N}^2(\text{C}^6\text{H}_5)_2\text{H}^+.\text{NO}_3^- \end{cases}$ , is prepared by the action of aniline on platosamidiammonium nitrate. It crystallises in very brilliant rhombic scales often having a faint rose tint, due to the presence of small quantities of resinous matter. It dissolves easily in hot water, and the concentrated solution solidifies in crystals on cooling.

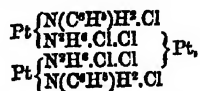
The *oxalate*,  $\text{Pt} \begin{cases} \text{N}^2\text{H}^+ \\ \text{NH}^2.\text{N}(\text{C}^6\text{H}_5)_2\text{H}^+ \end{cases} \left\{ \text{C}^2\text{O}^4 + \text{H}^2\text{O} \right\}$ , obtained by treating the nitrate with ammonium oxalate, is a crystalline powder containing 37.85 p.c. platinum (calc. 37.77).

When the chloride,  $\text{Pt} \begin{cases} \text{N}^2\text{H}^+.\text{Cl}^- \\ \text{NH}^2(\text{C}^6\text{H}_5)_2\text{H}^+.\text{Cl}^- \end{cases}$ , or the solution formed by boiling platosamidiamine with aniline, water, and a little alcohol, is evaporated on the water-bath, a strongly coloured residue is obtained; and this residue, when washed with alcohol, leaves a whitish crystalline powder, the solution of which in a small quantity of water deposits crystals which, when purified by repeated crystallisation, have the composition  $\text{Pt} \left\{ \begin{smallmatrix} (\text{NH}^2)^2 \\ \text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \end{smallmatrix} \right\} \text{Cl}_2$ . This chloride is analogous to the chloride of platamonodiammonium, and is formed by the abstraction of 1 mol. aniline from the chloride,  $\text{Pt} \left\{ \begin{smallmatrix} (\text{NH}^2)^2 \\ (\text{N}.\text{C}^6\text{H}_5.\text{H}^2)^2 \end{smallmatrix} \right\} \text{Cl}_2$ .

When the chloride,  $\text{Pt} \left\{ \begin{smallmatrix} (\text{NH}^2)^2 \\ \text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \end{smallmatrix} \right\} \text{Cl}_2$ , is treated with potassium iodide, ammonia is given off, and a yellow powder is precipitated having the composition  $\text{Pt} \left\{ \begin{smallmatrix} \text{NH}^2 \\ \text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \end{smallmatrix} \right\} \text{I}_2$ , analogous to iodide of platosammonium.

The radicle of this iodide may be supposed to be derived from the radicle,  $\text{Pt} \left\{ \begin{smallmatrix} \text{NH}^2.\text{NH}^2 \\ \text{N}(\text{C}^6\text{H}_5)_2\text{H}^2.\text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \end{smallmatrix} \right\}$ , by abstraction of the two external molecules,  $\text{NH}^2$  and  $\text{N}(\text{C}^6\text{H}_5)_2\text{H}^2$ , just as platosamine is derived from platosodiamine by loss of the two external molecules  $\text{NH}^2$ . The isomeric chloride,  $\text{Pt} \left\{ \begin{smallmatrix} \text{NH}^2.\text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \\ \text{NH}^2.\text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \end{smallmatrix} \right\}$ , to be presently described, behaves differently with potassium iodide, the two external molecules of aniline being given off, and platosammonium iodide,  $\text{Pt} \left\{ \begin{smallmatrix} \text{NH}^2.\text{I}^- \\ \text{NH}^2.\text{I}^- \end{smallmatrix} \right\}$ , being produced.

The *chloride*,  $\text{Pt} \left\{ \begin{smallmatrix} \text{N}^2\text{H}^+ \\ \text{N}(\text{C}^6\text{H}_5)_2\text{H}^2 \end{smallmatrix} \right\} \text{Cl}_2$ , unites with platinous chloride, forming the double salt:



analogous to chloroplatinite of platamonodiammonium or to the brown chloride discovered by Peyrone (iv. 674). This double salt forms chamois-coloured scales having a brilliant, almost metallic lustre.

The *sulphate*,  $\text{Pt} \left\{ \begin{smallmatrix} (\text{N}^2\text{H}^+)^2 \\ (\text{C}^6\text{H}_5\text{N})^2 \end{smallmatrix} \right\} \text{SO}_4$ , is formed by dissolving aniline in a boiling

solution of platosomidiammonium sulphate, and separates on cooling in colourless prismatic crystals, which easily give off part of their aniline.

**β.** The *chloride*,  $\text{Pt}\left\{\begin{smallmatrix} \text{NH}^3\cdot\text{N}(\text{C}^6\text{H}^5)\text{H}^2\cdot\text{Cl} \\ \text{NH}^3\cdot\text{N}(\text{C}^6\text{H}^5)\text{H}^2\cdot\text{Cl} \end{smallmatrix}\right.$ , is formed by heating platosammonium chloride,  $\text{Pt}(\text{NH}^3)^2\cdot\text{Cl}^2$ , with water, aniline, and a little alcohol, and separates from the resulting solution on cooling in thin, nacreous, very light and shining plates. Heated with nitromuriatic acid, it yields yellow crystals having the form of platinammonium chloride. With potassium iodide it forms a yellow precipitate of platosammonium iodide.

The *chloroplatinite*,  $\text{PtCl}_2[\text{NH}^3\cdot\text{N}(\text{C}^6\text{H}^5)\text{H}^2]^2\cdot\text{PtCl}_2$ , is immediately precipitated as a very sparingly soluble, charmois-coloured, crystalline powder.

The *nitrate*,  $\text{Pt}(\text{NH}^3\cdot\text{C}^6\text{H}^5\text{N})^2(\text{NO}^2)^2$ , obtained by the action of aniline on platosammonium nitrate, crystallises in thin very brilliant scales, freely soluble in hot, sparingly in cold water.

The *sulphate*,  $\text{Pt}(\text{NH}^3\cdot\text{C}^6\text{H}^5\text{N})^2\text{SO}^4$ , forms slightly coloured, very thin plates.

**POLLEN.** The following analysis of this substance has been made by W. v. Schneider (*Ann. Ch. Pharm.* clvii. 235; *Chem. Soc. J.* [2], x. 175).

Water	29.89	p.c.
Ash (chiefly alkaline phosphate)	3.08	"
Albumin and peptones	17.81	"
Sugar	25.12	"
Fat, fat acids, cerotic acid, myricin, oleic acid	8.98	"
Colouring matter	7.56	"
Cell-membrane	7.42	"
Pectin		"
	99.86	"

The proportion of wax appears to be very small, whence, as well as from experiments on the consumption of food consumed by bees, in comparison with the wax which they produce, Schneider concludes that bees secrete wax, and that it is not brought into the hive with the pollen which they collect.

**POLYCRASE.** See TANTALATES.

**POTASSIUM.** On the solubility of this metal in liquid ammonia, see AMMONIA (p. 60).

On the amalgam of potassium, see MERCURY (p. 786).

*Separation from Sodium.*—For this purpose T. Schlösing (*Compt. rend.* lxxiii. 1269) recommends the use of ammonium perchlorate, prepared by boiling a concentrated solution of sodium perchlorate with sal-ammoniac, whereby it is obtained in fine crystals. The solution of this salt boiled with nitromuriatic acid is instantly resolved into a mixture of perchloric, nitric, and hydrochloric acids, the perchloric acid decomposing the chlorides and nitrates of the alkalis, and converting them into perchlorates.

To apply this reaction to the separation of potassium and sodium, the solution of the bases, having been concentrated in a tared platinum crucible, is mixed with the perchloric acid solution prepared as above. The whole is then evaporated to dryness, or till white fumes begin to appear; the precipitated potassium perchlorate is washed several times with alcohol, and dissolved in a small quantity of water to separate a little adhering sodium-salt; the solution is evaporated to dryness; the residue again washed with alcohol; and the pure potassium perchlorate dried at 250° and weighed. Test experiments show that this method gives very exact results.

*Bromide.*—On impurities in the commercial salt, see *Jahresb. f. Chem.* 1870, 300. On the method of testing it, see Falières (*Chem. Centr.* 1872, 425; *Chem. Soc. J.* [2], xi. 191).

*Hydrate.*—For the preparation of pure potassium hydrate by Wöhler's method (iv. 700), E. Pollacci recommends the use of iron instead of copper, as the potash prepared with copper always contains cupric oxide.

**PREHNITE.** On the crystalline form of this mineral from the Radanthal, see A. Strong (*Jahresb. f. Mineralogie*, 1870, 314; *Jahresb. f. Chem.* 1870, 1808).

**PREHNITIC ACID**,  $\text{C}^{10}\text{H}^8\text{O}^4$ , and **PREHNOMALIC ACID**,  $\text{C}^{10}\text{H}^{10}\text{O}^4$ . Acids obtained by heating hydromellitic acid with strong sulphuric acid (*1st Suppl.* 811).

**PROPANE,  $C^3H^8$ .** On dibromo- and dichloropropane or methylbromacetol and methylchloracetol, see PROPYLENE BROMIDES and CHLORIDES (pp. 1016, 1017). On nitropropanes, see PARAFFINS (p. 895).

**PROPARGYL COMPOUNDS.** Ethyl propargylate or propargylic ether,  $C^3H^5OC^2H^5$ , was discovered in 1865 by Liebermann, who obtained it by the action of potassium ethylate on bromallylene, and of boiling alcoholic potash on allyl tribromide (1st Suppl. 958). This ether has been further investigated by Liebermann and Kretschner (*Ann. Ch. Pharm.* clviii. 230; *Chem. Soc. J.* [2], ix. 527); and propargylic alcohol,  $C^3H^5O$ , has been discovered by L. Henry, who has likewise examined several of its derivatives (*Deut. Chem. Ges. Ber.* v. 274, 449, 569; vi. 728; vii. 20, 761).

**Propargyl Alcohol,  $C^3H^5O$  or  $CH \equiv C-CH^2OH$ ,** is obtained, together with monobromallyl oxide, by the action of aqueous potash on monobromallyl alcohol,  $(C^3H^5BrO)$ . It is a colourless liquid of peculiar odour, boiling at  $114^\circ-116^\circ$ ; sp. gr. = 0.9628 at  $21^\circ$ . Vapour-density = 1.88 (calc. 1.93). It is easily decomposed by electronegative chlorides, bromides, &c., and unites with  $Br^2$ ,  $HI$ , and  $HCl$ . It precipitates ammoniacal silver and copper solutions, forming the compounds  $C^3H^5AgO$  and  $C^3H^5(Cu^2)O$ . With anhydrous baryta it forms the compound,  $(HOC^3H^5)^2Ba.C^3H^5O$ , which crystallises in small plates (Henry).

**Ethyl Propargylate,  $C^3H^5O$  or  $CH \equiv C-CH^2(OC^2H^5)$ .**—Liebermann a. Kretschner find that allyl tribromide is better adapted for the preparation of this ether than trichlorhydrin, as it is more easily decomposed and yields a larger product. At the completion of the reaction, which took five hours in the case of the tribromide of allyl and seven with the trichlorhydrin, the alcohol was distilled off, and the first portions, which contained the ether, collected apart, the receiver being changed as soon as the distillate ceased to give a precipitate with silver nitrate. This last fraction was again rectified in a similar manner. A concentrated solution of silver nitrate was now cautiously added to the alcoholic solution of propargylic ether, and on agitation it became filled with crystalline plates of the silver compound. On adding ammonia to the filtrate, a small additional quantity of silver propargylic ether was generally obtained in the amorphous state. The behaviour of dilute alcoholic solutions of propargylic ether towards silver nitrate was probably the cause why Linnemann (*Ann. Ch. Pharm.* cxxxix. 19) failed to detect it amongst the products of the action of alcoholic potash on trichlorhydrin. In order to prepare the pure ether from the silver compound, it was first treated with ammonia to render it amorphous, and then thoroughly washed. On distilling this compound with dilute sulphuric acid, drying with calcium chloride, and rectifying, the ether was obtained pure. The ether is likewise obtained by the action of boiling alcoholic potash on dichloroglycide,  $C^3H^4Cl^2$ , and on allylene dibromide,  $C^3H^4Br^2$ .

According to Henry (*Deut. Chem. Ges. Ber.* v. 274), it is best prepared by heating bromallyl oxide,  $C^3H^5OC^2H^4Br$ , with an equal weight of potassium hydrate, the yield being nearly equal to the calculated quantity. The greater part separates as an oil on addition of water, and the remainder may be obtained as a silver compound in the manner above described. To remove the last traces of alcohol and water it must be treated with sodium-amalgam.

**Ethyl Propargylate** is a mobile liquid lighter than water, and boiling at  $80^\circ$  (L. a. K.), at  $81^\circ-86^\circ$ , and has a specific gravity of 0.83 at  $7^\circ$  (Henry). It has a penetrating odour, is somewhat soluble in water, and in all proportions in alcohol. Bromine combines directly with it without evolution of hydrobromic acid, forming the compound  $C^3H^5Br^2O.C^2H^5$ , which is heavier than water. This compound is not acted upon by sodium-amalgam in aqueous solution, but in an alcoholic solution the ether is regenerated. It exhibits the reactions assigned by Markownikoff (*Jahresh. f. Chem.* 1865, 492) to the dibromide of allyl ether, and by Tollens (*Ann. Ch. Pharm.* clvi. 167) to the dibromide of allyl alcohol (L. a. K.).

With sodium it forms a white solid compound, containing  $C^3H^5Na.OC^2H^5$  (Henry). The crystalline silver compound of propargylic ether has the composition,  $2(C^3H^5Ag.OC^2H^5) + AgNO^3$ ; on treating it with ammonia, silver nitrate separates, and an amorphous silver compound is formed. An alcoholic solution of propargylic ether mixed with an ammoniacal solution of silver chloride yields a white, curdy precipitate,  $2(C^3H^5Ag.OC^2H^5) + AgCl$ , which gradually gives up silver chloride to ammonia, and is resolved by nitric acid into propargylic ether and silver chloride, whilst silver passes into solution.

A copper compound,  $(C^3H^5.OC^2H^5)^2(Cu^2)$ , is formed by precipitation with ammoniacal solution of cuprous chloride, as an amorphous, yellow precipitate. Cuprous chloride without ammonia also forms an amorphous precipitate. Respecting the constitution of these metallic derivatives, see *Chem. Soc. J.* [2], ix. 529.

**Methyl Propargylate**,  $C^4H^5OCH^3$ , is obtained by heating methylbromallyl ether,  $CH^3OC^4H^5Br$ , with alcoholic potash; also, together with methylbromallyl ether, by heating the dibromide of methylallyl ether with solid potassium hydrate. It boils at  $61^\circ-62^\circ$  (Henry).

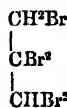
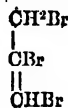
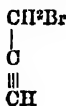
**Amyl Propargylate**,  $C^4H^5OC^5H^{11}$ , obtained in like manner, is a limpid, nearly scentless liquid boiling at  $140^\circ-145^\circ$ .

**Propargyl Bromides**.—The *monobromide*,  $C^4H^5Br$  or  $CH \equiv C-CH^2Br$ , is formed, together with  $C^4H^4Br^2$ , by treating propargyl alcohol with phosphorous bromide; it is a liquid boiling at  $88^\circ-90^\circ$ , and having a sp. gr. of 1.59 at  $11^\circ$ , 1.52 at  $20^\circ$  (Henry).

The *tribromide*,  $C^4H^3Br^3$ , prepared by direct addition of bromine to the monobromide, is a colourless, non-volatile liquid, having a sp. gr. of 2.53 at  $10^\circ$ .

The *pentabromide*,  $C^4HBr^5$ , formed in like manner from the tetrabromide, is a thick non-volatile liquid having a sp. gr. of 3.01 at  $10^\circ$ .

These three bromides may be represented by the following formulæ:



**Propargyl Iodide** is produced by the action of iodine and red phosphorus on the alcohol; it boils at about  $120^\circ$ , but decomposes at the same time.

**Propargyl Acetate** is readily obtained by acting on the alcohol with acetyl chloride. It boils at  $124^\circ-125^\circ$ , has a sp. gr. 1.0031 at  $12^\circ$  and a disagreeable odour.

**Propargyl Sulphocyanate**,  $C^4H^5SCN$ , is easily produced by the action of the bromide on an alcoholic solution of potassium sulphocyanate. It is an oily liquid, smelling like mustard-oil, and decomposed by heat.

**Dipropargyl**, or **Diallylenyl**,  $C^4H^4$  (L. Henry, *Deut. Chem. Ges. Ber.* vi. 955-963). When diallyl tetrabromide is distilled with a large excess of caustic potash or soda, it loses 2 mols. of hydrobromic acid, and *dibromodiallyl*,  $C^4H^4Br^2$ , is formed, some of which, by the further loss of hydrobromic acid, is converted into dipropargyl. This isomeride of benzene is a mobile, limpid liquid, having a high refractive index and an odour like that of propargylic ether, but more intense and penetrating. It boils at about  $85^\circ$ , has at  $18^\circ$  the sp. gr. 0.81, and burns with a luminous and smoky flame. It is easily distinguished from benzene by its property of combining with explosive violence with bromine, forming the *tetrabromide*,  $C^4H^4Br^4$ , a viscid liquid, having a faint smell and bitter taste. Sp. gr. = 2.460 at  $19^\circ$ . When heated it gives off hydrobromic acid, and leaves a carbonaceous residua. It combines in the dark with more bromine, forming probably the *octobromide*,  $C^4H^4Br^8$ . Dipropargyl gives, with an ammoniacal solution of cuprous chloride, a greenish-yellow precipitate, which, when dried over sulphuric acid, or at  $90^\circ-100^\circ$ , has the composition  $C^4H^4Cu^2 + 2H^2O$ . It explodes at about  $100^\circ$ , and when touched with a flame, burns with a scintillating green flame. The silver-compound,  $C^4H^4Ag^2 + 2H^2O$ , is obtained as an amorphous white precipitate by adding the hydrocarbon to an aqueous solution of silver nitrate; in the light it soon becomes pink, and then black. It explodes below  $100^\circ$ , leaving a residue of carbon and silver.

The constitution of dipropargyl or diallylenyl may be expressed by the formula,  $HC \equiv C-CH^2-CH^2-C \equiv CH$ , which explains why it forms compounds containing 2 atoms of a metal, while in allylene,  $CH \equiv C-CH^2$ , only 1 atom of hydrogen can be replaced.

The propargyl-compounds boil  $18^\circ-20^\circ$  higher than the corresponding allyl-compounds; dipropargyl ought, therefore, to boil at about  $95^\circ-100^\circ$ , but it actually boils at  $85^\circ$ . Diallyl makes, however, a similar exception, for while the allyl-compounds boil at the same temperature as the normal propyl-compounds, the hydrocarbon boils at the same temperature as di-isopropyl, or  $10^\circ$  lower than normal dipropyl.

**Dipropargyl Tetrabromide**,  $C^4H^4Br^4$ , is a viscid liquid having a faint smell and bitter taste. Sp. gr. = 2.460 at  $19^\circ$ . When heated it gives off hydrobromic acid and leaves a carbonaceous residue.

**Octobromide**,  $C^4H^4Br^8$ .—Formed by addition of bromine to the tetrabromide; very little hydrobromic acid is evolved, and in a few minutes the mass becomes solid and crystalline. Thus produced, the octobromide is a granular crystalline powder, but by spontaneous evaporation of its solution in carbon sulphide, distinct rhombohedrons of considerable size may be obtained. It is colourless, strongly refractive, and smells slightly of camphor. It melts at  $140^\circ-141^\circ$ , and solidifies at  $180^\circ$ . It is not volatile.



**PROPIONAMIDE**,  $C^3H^5O.NH^2$  (F. Sestini, *Cimento*, iv. 21). This compound is best prepared by mixing ethyl propionate with 5-6 times its volume of strong ammonia, leaving the liquid to stand for 3-4 days, and shaking the mixture from time to time. The liquid is first concentrated on the water-bath, and then evaporated over sulphuric acid to the consistence of a syrup, which is exhausted with ether, the solution evaporated, and the residue recrystallised from ether or chloroform.

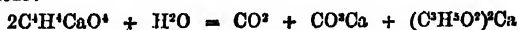
Propionamide is colourless, readily soluble in cold alcohol and ether, from which it crystallises in radiate crystalline masses, or in prisms grouped in fascicles; from chloroform it crystallises in pearly scales. It melts at  $76^{\circ}$ - $76^{\circ}$ , and solidifies again at  $50^{\circ}$ ; at a higher temperature it sublimes.

**Propionamide Hydrochloride**,  $(C^3H^5ONH^2)^2ClH$ , is obtained by passing hydrochloric acid gas into an ethereal solution of the amide; the liquid separates into two layers, the lower of which contains the hydrochloride, which is isolated by washing several times with ether and evaporating over sulphuric acid. It crystallises in needles very sparingly soluble in ether, readily soluble in water and alcohol, and having an acid reaction.

**Mercury-propionamide**,  $(C^3H^5O.NH)^2Hg$ , is obtained in large colourless quadrate plates by heating an aqueous solution of the amide with mercuric oxide to  $50^{\circ}$ , and leaving the solution to evaporate slowly; it dissolves sparingly in cold, readily in boiling water.

**Propionanilide**,  $C^3H^5O.NH.C^6H^5$ , was obtained by adding drop by drop 3 pts. of propionyl chloride to 10 pts. of well-cooled aniline. It crystallises from water in small micaceous plates which melt at  $92^{\circ}$ ; at a higher temperature it sublimes partially. By boiling it with acids or alkalis, it is decomposed into propionic acid and aniline.

**PROPIONIC ACID**,  $C^3H^5O^2 = C^3H^5.CO^2OH$ . *Formation*.— $\alpha$ . By oxidising allylene with aqueous chromic acid (Berthelot, *Ann. Ch. Phys.* [4], xxiii, 212).  $\beta$ . By the combination of carbon monoxide with potassium ethylate:  $CO + C^2H^5OK = C^3H^5.CO^2K$  (Hagemann, *Deut. Chem. Ges. Ber.* iv. 877).  $\gamma$ . By the fermentation of calcium succinate in contact with microzyme chalk (1st *Suppl.* 614), and a small quantity of meat:



(Béchamp, *Compt. rend.* lxx. 999).

*Preparation*.—1. *By Oxidation of Normal Propyl Alcohol*. Pierre a. Puchot (*Ann. Chim. Phys.* [4], xxviii. 71) add a mixture of propyl alcohol, water, and sulphuric acid to a solution of potassium dichromate to which sulphuric acid has been added. The reaction being terminated, the mixture yields dilute propionic acid on distillation. In order to obtain the acid in a concentrated form, its potassium salt is treated with sulphuric acid diluted with a small quantity of water, the whole being kept for some time at a temperature of about  $80^{\circ}$ , when the propionic acid separates as a yellowish liquid which may be decanted from the saline residue. The crude acid thus obtained crystallises on cooling, but after distillation it no longer possesses the property of crystallising at the ordinary temperature, the crystallisation being apparently facilitated by the presence of a small quantity of potassium bisulphate. The acid liquid thus obtained yields, on fractionation, pure propionic acid,  $C^3H^5O^2$ .

2. *From Lactic Acid by the action of Hydriodic Acid*.—This reaction, discovered by Lautmann (iv. 730), is recommended by A. Fround (*J. pr. Chem.* [2], v. 446) as a convenient mode of preparation. 60 grams of iodine suspended in 140 grams of water are converted into hydriodic acid by means of sulphuric acid, and the hydriodic acid thus obtained is placed in a retort with 60 grams of lactic acid, after which the mixture is distilled until about 100 grams of liquid have passed over. A condensing tube being now adapted to the apparatus, the contents of the retort are digested for about four hours, when the iodine, which by this time has crystallised in the condensing tube, is washed back into the retort with the 100 grams of distillate previously drawn off, and sulphuric acid is passed through the mixture in order to rehydrogenise the free iodine. The deposited sulphur being removed, 100 grams are again distilled off, the contents of the retort are digested for another period of four hours, and his series of operations is repeated six or seven times, the whole of the lactic acid being by this time converted into propionic acid; almost the whole of which is contained in the 100 grams drawn off after the last digestion. This distillate is now mixed with 50 grams of water, and distilled as long as the liquid which passes over produces a perceptible turbidity in a solution of lead propionate. The nearly pure solution of propionic acid thus obtained is neutralised with sodium carbonate, mixed with lead propionate to remove small quantities of iodine, then filtered and evaporated to 2nd *Sup.*

dryness, and the dry sodium propionate is fused, pulverised, and decomposed by a stream of dry hydrochloric acid gas as recommended by Linnemann (*Ann. Ch. Pharm.* cxlviii. 251). The propionic acid thus liberated is distilled off and freed from hydrochloric acid by passing a stream of dry air through it.

Lactic acid thus treated yields from 61 to 62 p.c. pure propionic acid. No acetic acid is formed in the process, the only secondary products being small quantities of aldehyde and a gas which burns with a bluish flame.

**Properties.**—Pure propionic acid boils at  $139^{\circ}$  (Fround), at  $140.71^{\circ}$  (corrected and reduced to 760 mm. pressure: Linnemann), at  $141.5^{\circ}$  under the same pressure (Pierre a. Puchot). Sp. gr. = 0.9961 at  $19^{\circ}$  (Linnemann), 1.0143 at  $0^{\circ}$ , 0.9607 at  $49.6^{\circ}$ , and 0.9062 at  $99.8^{\circ}$  (Pierre a. Puchot). Its odour recalls that of glacial acetic acid and that of butyric acid (Pierre a. Puchot). It mixes in all proportions with water, is optically inactive, and does not solidify at  $-21^{\circ}$ . It is not separated from its aqueous solution by salts, or even by phosphoric acid, and only the concentrated acid is partially dehydrated by calcium chloride, a considerable quantity of hydrochloric acid being at the same time set free and lime dissolved. The dry acid quickly absorbs water from the air (Linnemann, *Ann. Ch. Pharm.* clx. 195).

**Propionates.**—The neutral ammonium salt,  $C^3H^5O^2(NH^4)$ , forms long slender prisms, very deliquescent, easily soluble in water, insoluble in ether. When its concentrated solution is left over sulphuric acid, an acid salt,  $C^3H^4O^2(NH^4).C^3H^4O^2$ , crystallises out in small quadratic plates. On distilling the neutral salt, the acid salt passes over, crystallising in six-sided plates which melt at  $45^{\circ}$  (Sestini).

The silver salt,  $C^3H^4O^2Ag$ , crystallises from cold or from hot solution in shining leaflets, or in large broad shining needles, according to the degree of concentration (Linnemann); in masses of fine silky anhydrous needles which execute gyratory movements during the process of solution in water (Pierre a. Puchot). Dissolves in 119 pts. of water at  $19^{\circ}$ , and is anhydrous at  $100^{\circ}$  (Linnemann).

The barium salt may be obtained in large crystals by allowing its solution to evaporate spontaneously, or as a granular powder consisting of small crystals by cooling a hot solution. The crystals dried by the heat of the sun contain  $(C^3H^4O^2)^2Ba.H^2O$  (Pierre a. Puchot). The salt is anhydrous at  $100^{\circ}$ , and crystallises by evaporation over sulphuric acid in scales which dissolve in 1.67 pt. water at  $17^{\circ}$ .

The calcium salt crystallises when its concentrated solution is left over sulphuric acid in transparent laminae which dissolve in 1.87 pt. water at  $17^{\circ}$ , and when dried at  $100^{\circ}$  have the composition  $(C^3H^4O^2)^2Ca.H^2O$ .

The neutral lead salt,  $(C^3H^4O^2)^2Pb$ , is easily soluble and remains as a gummy mass when its aqueous solution dries up. The very characteristic basic lead salt is always formed when propionic acid or the neutral salt is triturated with excess of litharge and water, and the mixture is dried over the water-bath. If the residue be drenched with cold water, and the filtered solution heated to boiling or evaporated at the boiling heat, the salt separates suddenly and almost completely on stirring, the solution sometimes becoming nearly solid. Dried over sulphuric acid it has the composition  $3(C^3H^4O^2)^2Pb + 4PbO$ . It separates in needles or as a crystalline powder, which gradually dissolves in 8–10 pts. of water at  $14^{\circ}$ . This salt affords a ready means of separating propionic acid from formic, acetic, and acrylic acid. The solution mixed with lead oxide and water is evaporated to dryness, the residue is exhausted with cold water, and the basic lead propionate is precipitated by heating the solution. Pseudo-propionic or butyric acid does not exhibit this reaction (Linnemann, *loc. cit.*)

**Ethyl Propionate.**  $C^3H^5O.C^2H^5$ , is most easily prepared by distilling a mixture of 24 pts. alcohol of 96 p.c., 18 pts. propionic acid and 4 pts. sulphuric acid (Sestini).

**Bromopropionic Acids.** *Dibromopropionic acid*,  $C^3H^2Br^2O^2$ .—Three modifications of this acid are possible, viz.:



and of these, the second and third, distinguished as  $\alpha$  and  $\beta$ , are known.

*$\alpha$ -Dibromopropionic acid* (Friedel a. Machuca, *Compt. rend.* liv. 220; Philipp a. Tollens, *Deut. Chem. Ges. Ber.* vi. 515). This modification is formed by the action of bromine, at  $140^{\circ}$ , on monobromopropionic acid,  $CH^2Br-COOH$ , and must therefore be represented by the second or third of the preceding formulae; the second, however, belongs, as will be presently seen, to the  $\beta$ -modification; consequently the  $\alpha$ -acid must be represented by the third.

This acid when pure forms microscopic rectangular plates, melting at  $65^{\circ}$  (Friedel

a. Machuca), at  $61^{\circ}$  (Philippi a. Tollens). A mixture of the  $\alpha$ - and  $\beta$ -acids remains liquid for a long time, and only after some weeks yields very deliquescent microscopic cubes (P. a. T). The  $\alpha$ -acid distils at  $227^{\circ}$  (at  $220^{\circ}$ - $221^{\circ}$  according to Tollens) with slight decomposition. Silver oxide, in presence of water, transforms it into a non-brominated acid, the calcium salt of which is precipitated by alcohol (Friedel a. Machuca). Treated with zinc and sulphuric acid, it is converted into propionic acid (Philippi a. Tollens).

*Barium Dibromopropionate*,  $(C^2H^3Br^2O^2)^2Ba + 9H^2O$ , forms efflorescent needles which give off all their water at  $90^{\circ}$ . The *calcium salt*,  $(C^2H^3Br^2O^2)^2Ca + 2H^2O$ , forms silky needles which also give off their water at  $90^{\circ}$ .

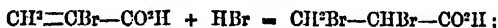
*Ethyl Dibromopropionate*,  $C^2H^3Br^2O^2.C^2H^5$ , obtained by the action of hydrochloric acid gas on an alcoholic solution of the acid, forms a liquid of camphorous odour, boiling at  $190^{\circ}$ - $191^{\circ}$ , and having a specific gravity of 1.7536 at  $12^{\circ}$  (Philippi a. Tollens).

*$\beta$ -Dibromopropionic acid*,  $CH^2Br-CHBr-COOH$  (Münder a. Tollens, *Deut. Chem. Ges. Ber.* v. 73; *Ann. Ch. Pharm.* clxvii. 222).—This acid is formed by the oxidation of the so-called dibromide of allyl alcohol,  $C^3H^4Br^2O$  (p. 48), which is really a glyceric dibromhydrin or a dibromopropyl alcohol. This compound, gently heated with nitric acid of sp. gr. 1.4-1.48, yields the dibrominated acid in crystals, or if stronger nitric acid is used, as an oil which solidifies when dried in the water-bath. The crystals are purified by draining, washing with a little water, pressing between bibulous paper, then melting them, and leaving the fused mass to solidify, again washing, pressing, melting, &c., and repeating this treatment till the acid melts constantly at  $62^{\circ}$ - $64^{\circ}$ .

The formation of  $\beta$ -dibromopropionic acid from allyl alcohol dibromide is represented by the equation:



It is also formed by heating  $\alpha$ -monobromacrylic acid with 3 or 4 pts. of hydrobromic acid to  $100^{\circ}$ :



and, lastly, from  $\alpha$ -dibromopropionic acid, by heating with hydrobromic acid to  $100^{\circ}$  for a week. This remarkable example of a molecular change may be explained by supposing that the  $\alpha$ -acid, which at  $120^{\circ}$  is quickly resolved into hydrobromic acid and  $\alpha$ -bromacrylic acid, undergoes the same change slowly at  $100^{\circ}$ ; thus:



and that the hydrobromic acid then acts on the bromacrylic acid in the manner above mentioned (Philippi a. Tollens, *Ann. Ch. Pharm.* clxxi. 333).

$\beta$ -Dibromopropionic acid forms rhombic or prismatic crystals belonging to one of the oblique systems. Its melting point is higher than that of the  $\alpha$ -acid ( $61^{\circ}$  according to Tollens). It boils with partial decomposition at  $220^{\circ}$ - $240^{\circ}$ . When quite pure it smells like propionic acid; the impure acid has a pungent odour and blisters the skin more strongly than the pure acid. 1 pt. of water at  $11^{\circ}$  dissolves 19.45 pts. of the acid; calcium chloride and nitric acid separate it from the aqueous solution. 1 pt. of ether at  $10^{\circ}$  dissolves 3.04 pts. of the acid. Alcohol dissolves it freely. It is not deliquescent.

$\beta$ -Dibromopropionic acid heated with *alcoholic potash* is converted into bromacrylic acid:



Treated with *sine* and *dilute sulphuric acid*, it gives up 2 at. bromine and is converted into acrylic acid—



(Wagner a. Tollens, *Deut. Chem. Ges. Ber.* vi. 513; *Ann. Ch. Pharm.* clxxi. 340).

When *ammonia* is passed into its aqueous solution, laminar crystals separate which have the composition of ammonium amidobromopropionate,  $C^2H^3Br(NH^2)O^2.NH^4$  (Münder a. Tollens).

*Dibromopropionates*.—The potassium salt,  $C^2H^3Br^2O^2K$ , forms tabular crystals. The *silver salt*,  $C^2H^3Br^2O^2Ag$ , is a white, microscopically crystalline precipitate. The *calcium salt*,  $(C^2H^3Br^2O^2)^2Ca + 2H^2O$ , obtained by neutralisation, crystallises from alcohol in silky needles which effloresce over sulphuric acid. The *strontium salt* crystallises in flexible needles about half an inch long. The *lead salt* is basic and contains 14.23 p.c. lead.

The *methylic ether*,  $C^2H^3Br^2O^2.CH^3$ , prepared by saturating the solution of the acid

in methyl alcohol with hydrochloric acid, and separated by water, boils at  $203^{\circ}$  under a pressure of 745 mm. It is colourless, slightly oily, and has a fruity odour. The ethylic ether,  $C^2H^5Br^2O^2.C^2H^5$ , is colourless, has a somewhat fruity odour when dilute, boils at  $211^{\circ}$ – $214^{\circ}$  under a pressure of 746 mm., and has a density of 1.796 at  $0^{\circ}$ , 1.777 at  $15^{\circ}$ . The allylic ether,  $C^2H^5Br^2O^2.C^3H^5$ , has a disagreeable odour; boils at  $215^{\circ}$ – $220^{\circ}$  under a pressure of 745 mm. Sp. gr. = 1.843 at  $0^{\circ}$ ; 1.818 at  $20^{\circ}$  (Mündor a. Tollons).

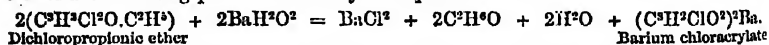
**Chloropropionic Acids.** Only one modification of monochloropropionic acid is at present known, viz. the  $\alpha$ -acid,  $CH^3-CHCl-CO^2H$ . The acid produced by the action of phosphorus pentachloride on glyceric acid, and supposed by Wichelhaus to consist of  $\beta$ -chloropropionic acid (1st Suppl. 960), has been shown by Werigo a. Werner (Ann. Ch. Pharm. clxx. 163) to be a chlorinated acrylic acid.

$\alpha$ -Chloropropionic acid boiled with aqueous ammonia yields a large quantity of lactic acid, together with alanine. Alcoholic ammonia acts very slowly on the acid, but when its action is strengthened by the addition of a little concentrated aqueous ammonia, alanine and ethyl-lactic are formed, together with lactic acid. When  $\alpha$ -chloropropionic acid is heated with alcohol,  $\alpha$ -chloropropionic ether is formed, but no ethyl-lactic acid (W. Heintz, Ann. Ch. Pharm. clvi. 25).

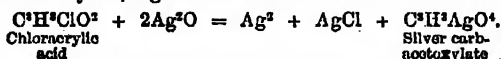
**Dichloropropionic acid**,  $C^2H^2Cl^2O^2$ .—Of this acid there are two modifications analogous to those of dibromopropionic acid.

$\alpha$ -Dichloropropionic acid,  $CH^3-CCl^2-COOH$ .—The ethylic ether of this acid is obtained by the action of alcohol on the chloride formed by the action of phosphorus pentachloride on pyracemic acid,  $CH^3-CO-CO^2H$ . This ether,  $CH^3-CCl^2-COOC^2H^5$ , is a colourless liquid having a pleasant odour of apples, a specific gravity of 1.2493 at  $0^{\circ}$ , and boiling at  $160^{\circ}$ . Heated to  $130^{\circ}$  with water it yields pyracemic acid. Dilute ammonia converts it into dichloropropionamide,  $C^2H^2Cl^2O.NH^2$ , which is soluble in alcohol, crystallises in large rectangular leaflets melting at  $116^{\circ}$ , and volatilising before fusion when heated in an open vessel. The ether treated with boiling milk of lime yields an acid which, from the composition of its calcium and barium salts, appears to be carbacetoxylic acid,  $C^2H^2O^4$  (Klimenko, Deut. Chem. Ges. Ber. iii. 465; v. 477).

$\beta$ -Dichloropropionic acid,  $CH^3Cl-CHCl-COOH$ , is formed by the action of water on the crude product obtained by treating glyceric acid with phosphorus pentachloride. This product contains the chloride,  $C^2H^2Cl^2OCl^2$ , and when treated with alcohol yields ethyl  $\alpha$ -dichloropropionate, which boils at  $180^{\circ}$ – $190^{\circ}$ . This ether dissolves without residue in baryta water even when dilute, and on removing the excess of baryta with carbonic acid and evaporating the solution, either in a vacuum or at a temperature not exceeding  $70^{\circ}$ , the barium salt,  $C^2H^2Cl^2Ba + 11H^2O$ , is obtained in mammellated crystals. The solution of this salt is decomposed by alcohol and ether. The dried crystals become heated in contact with water. By treating this salt with silver sulphate, removing the excess of the latter with barium hydrate, and the excess of baryta with carbonic acid, barium chloracrylate,  $(C^2H^2ClO^2)^2Ba$ , is obtained, its formation taking place as shown by the equation:



The decomposition of this barium salt by sulphuric acid yields chloracrylic acid, which crystallises in small radiate needles, is very volatile at ordinary temperatures, has a strong and peculiar odour, and melts at  $65^{\circ}$ . These are the properties which Wichelhaus ascribed to his  $\beta$ -chloropropionic acid. This acid, treated with silver oxide, yields silver carbacetoxylic acid, together with metallic silver and silver chloride:



The decomposition of ethyl dichloropropionate may also yield an acid, probably having the composition of monochlorolactic acid (Werigo a. Werner, Ann. Ch. Pharm. clxx. 163).

**PROPYL ALCOHOLS and ETHERS.** *Normal Propyl Alcohol*,  $CH^3-CH^2-CH^2OH$ .—The most important results of recent investigations on the formation, preparation, and properties of this alcohol are given in the 1st Suppl. pp. 963, 964. Rossi's method of preparing it from ethyl alcohol is described in detail in the *Gazzetta chimica italiana*, i. 230–239, and a full abstract of the paper is given in the *Journal of the Chemical Society*, [2], ix. 1030.

Linnemann (Ann. Ch. Pharm. clxi. 18) prepares normal propyl alcohol from propionic acid by distilling a mixture of pure and dry propionate and formate of calcium, and reducing the propionic aldehyde thus obtained with sodium amalgam.

Linnemann's method of separating normal propyl alcohol and isobutyl alcohol from a mixture of fermentation alcohols by means of his apparatus for fractional distillation (p. 486) is described in *Ann. Ch. Pharm.* clx. 105; abstr. *Zeitschr. f. Chem.* [2], vii. 675; *Jahresh. f. Chem.* 1871, 397. For Pierre a. Puchot's method of effecting this separation, see *Compt. rend.* lxx. 406; *Jahresh.* 1870, 421.

Allyl alcohol, heated with potassium hydrate, yields a mixture of alcohols, which, when converted into bromides and fractionated, gives a mixture of ethyl and propyl bromides, and the latter, when oxidised, yields propionic acid, with scarcely a trace of carbonic acid, showing that the allyl alcohol has been converted into normal propyl alcohol free from the iso-alcohol (Tollens, *Zeitschr. f. Chem.* [2], vii. 242).

According to Linnemann (*Ann. Chem. Pharm.* clxi. 26) pure normal propyl alcohol, prepared by distilling propyl benzoate with aqueous potash, boils at  $97.41^{\circ}$  and has a sp. gr. of 0.8066 at  $15^{\circ}$ .

Respecting the conversion of normal propyl alcohol into isopropyl alcohol, see below.

**Normal Propyl Bromide**,  $\text{CH}^3\text{--CH}^2\text{--CH}^2\text{Br}$ , boils, according to Pierre a. Puchot (*J. Pharm.* [4], xiii. 9) at  $72^{\circ}$ , and has a sp. gr. of 1.3197 at  $0^{\circ}$ , 1.301 at  $15^{\circ}$ , 1.2599 at  $54.2^{\circ}$ , the coefficient of expansion increasing with the temperature. According to Linnemann (*loc. cit.*) it boils at  $70.82^{\circ}$ , and has a sp. gr. of 1.3507 at  $16^{\circ}$ .

**Monobromopropyl Bromide**,  $\text{C}^3\text{H}^6\text{Br}^2 = \text{CH}^3\text{Br--CH}^2\text{--CH}^2\text{Br}$ , is formed by heating 5 grams of propyl bromide and 6.5 grams of bromine for four hours to  $130^{\circ}\text{--}140^{\circ}$ . It boils at  $141^{\circ}\text{--}161^{\circ}$ , and has a density of 1.9463 at  $17^{\circ}$ . With acetic acid and zinc it yields propylene. Heated with 6 vols. water to  $200^{\circ}$  for six hours, it is decomposed, yielding hydrobromic acid and acetone. From these reactions it appears to be identical with the propylene dibromide formed by the action of bromine on isopropyl bromide (Linnemann, *loc. cit.*)

**Propyl Chloride**,  $\text{C}^3\text{H}^7\text{Cl}$ , is a limpid colourless liquid having a sweet though slightly ulliaceous odour. Boils at  $46.5^{\circ}$ . Sp. gr. 0.9156 at  $0^{\circ}$ , 0.8918 at  $19.75^{\circ}$ , 0.8671 at  $39^{\circ}$  (Pierre a. Puchot, *Ann. Chim. Phys.* [4], xx. 234; *Jahresh. f. Chem.* 1871, 372; *Chem. Soc. J.* [2], ix. 808). Linnemann, by heating propyl iodide with iodine monochloride, obtained propyl chloride boiling at  $46.36^{\circ}$ , and having a sp. gr. of 0.9160 at  $18^{\circ}$ ; by heating the iodide with mercuric chloride to  $130^{\circ}\text{--}140^{\circ}$ , propyl chloride was obtained boiling at  $46.44^{\circ}$ , and having a sp. gr. of 0.8959 at  $19^{\circ}$ .

**Propyl Iodide**,  $\text{C}^3\text{H}^7\text{I}$ , obtained by treating the pure alcohol with anhydrous hydriodic acid, is a mobile liquid smelling like ethyl iodide, and boiling at  $192.2^{\circ}$ . Sp. gr. at  $16^{\circ} = 1.7610$ . It is not changed by heating with fuming hydriodic acid to  $150^{\circ}$ , but when it is heated with 6 vols. of water to  $100^{\circ}$  for 24 hours, about 36 p.c. is converted into propyl alcohol and hydrogen iodide. By the action of silver oxide or mercuric oxide on a solution of the iodide in glacial acetic acid at  $100^{\circ}$ , a small quantity of propylene is formed, besides propyl oxide, propyl acetate, and propyl alcohol. Not a trace of an isopropyl compound was formed in any of these decompositions (Linnemann).

**Propyl Oxide**,  $(\text{C}^3\text{H}^7)^2\text{O}$ , smells like ethyl oxide and boils at  $82^{\circ}\text{--}86^{\circ}$  (Linnemann).

**Propyl Acetate** is a mobile liquid, smelling like acetic ether, and at the same time like fruit. Boiling point,  $101.98^{\circ}$ ; sp. gr. at  $15^{\circ} = 0.8992$ .

**Propyl Propionate** has a faint but pleasant odour, like that of pears. Boiling point  $122.44^{\circ}$ ; sp. gr. at  $13^{\circ} = 0.8885$ .

**Propyl Butyrate** smells like other butyric ether. Boiling point,  $143.42^{\circ}$ ; sp. gr. at  $15^{\circ} = 0.8789$ .

**Propyl Benzoate** is a thick, colourless, refractive liquid, possessing hardly any smell at the common temperature, but its vapour is irritating and produces coughing. Boiling point,  $229.47^{\circ}$ ; sp. gr. at  $16^{\circ} = 1.0316$  (Linnemann).

**Boropropyllic Ether**.—When a current of pure boron chloride is passed very slowly into anhydrous propyl alcohol at  $0^{\circ}$ , the gas is absorbed, and two layers of liquid are formed. The upper layer, after purification, yields *boropropyllic ether* (or *propoxyl boride*),  $\text{B}(\text{OC}^3\text{H}^7)^2$ , which is a colourless, mobile liquid, having a density of 0.807 at  $16^{\circ}$ , boiling at  $172^{\circ}\text{--}175^{\circ}$ . When applied to the tongue it causes a burning sensation and leaves a slightly bitter after-taste. Alcohol, ether, and water dissolve it readily. The aqueous solution decomposes, boric acid being deposited. Propoxyl boride burns with a green-edged flame, dense fumes of boric acid being at the same time evolved (Cahours, *Compt. rend.* lxxvi. 1383).

**Propyl Allophanate**,  $\text{C}^3\text{H}^{10}\text{N}^2\text{O}^3 = \text{C}^3\text{H}^8\text{N}^2\text{O}^2.\text{C}^3\text{H}^7$ , is produced, together with propyl urethane, by the action of propyl alcohol on urea. It forms pearly laminae slightly soluble in cold water, very soluble in hot water and in alcohol (Cahours).

*Propyl Carbamate* or *Propyl-urethane*,  $C^3H^7O = CO.NH^2.OC^3H^7$ , formed at the same time, according to the equation :

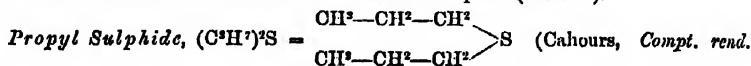


may be separated from the excess of urea by digesting with ether, evaporating the ethereal solution to dryness, dissolving in a little water, and evaporating the aqueous solution. It forms long, colourless, shining prisms, readily soluble in water or alcohol. It melts at  $51^{\circ}-53^{\circ}$ , and boils at  $104^{\circ}-106^{\circ}$  (Cahours).

*Tripropyl Biuret*,  $CON^2(C^3H^7)^2.CONH^2$ .—When a mixture of potassium propyl-sulphate and potassium cyanate is distilled, propylene is given off, and a yellowish solid distillate is obtained which, after crystallisation from alcohol, is found to have the composition of this substance (Roemer).

*Propyl Sulphydrate* or *Propyl Mercaptan*,  $C^3H^7S = CH^2-CH^2-CH^2SH$ , is obtained by digesting normal propyl bromide with an alcoholic solution of potassium sulphhydrate, distilling the product, and adding water to the distillate. Under these circumstances the mercaptan is precipitated as a colourless mobile liquid, having the characteristic odour of mercaptans. It boils at  $67^{\circ}-68^{\circ}$ , is not quite insoluble in water, and unites with freshly precipitated mercuric oxide, forming the mercaptide  $(C^3H^7S)^2Hg$ , which crystallises in shining leaflets melting at  $68^{\circ}$  (H. Roemer, *Deut. Chem. Ges. Ber.* vi. 785).

*Propyl-disulphocarbonic Acid*.—The potassium salt of this acid is obtained in shining yellow needles by adding carbon disulphide to a solution of potassium hydrate in normal propyl alcohol, and crystallising the yellowish mass which is deposited. The addition of an acid to the potassium salt causes the separation of free propyl disulphocarbonic acid in the form of an oil which soon decomposes (Roemer).



lxxvi. 133).—This compound is readily obtained by heating potassium monosulphide with iodide or chloride of propyl in alcoholic solution, the action being completed at the temperature of the water-bath in sealed tubes. Most of the alcohol is evaporated off, and the residue treated with water, which leaves undissolved a fetid oil lighter than water, boiling at  $130^{\circ}-135^{\circ}$  after dessication with anhydrous calcium chloride, and of specific gravity 0.814 at  $17^{\circ}$ .

When treated with propyl iodide and a little water in sealed tubes, this sulphide gives rise to a sulphine-iodide,  $S(C^3H^7)^2I$ , and this iodide, treated successively with silver oxide, hydrochloric acid and platinum chloride, yields a platino-chloride containing  $[S(C^3H^7)^2Cl]^2PtCl_4$ .

Similarly, propyl iodide combines with the sulphides of ethyl and methyl, giving rise to the compounds  $S(C^2H^5)^2I$  and  $S(C^2H^5)(CH^3)^2I$ , which form the platino-chlorides—



and the iodides of ethyl and methyl combine with propyl sulphide to form analogous compounds.

**METALLIC COMPOUNDS OF PROPYL** (Cahours, *Compt. rend.* lxxvi. 133, 1383).

*Mercury-propyl*.—When propyl iodide is treated by Frankland & Duppa's process (action of sodium amalgam in presence of acetic ether), mercury-propyl is obtained, forming a liquid insoluble in water, slightly soluble in alcohol, and readily soluble in ether, boiling at  $189^{\circ}-191^{\circ}$ , and having the specific gravity 2.124 at  $16^{\circ}$ . Iodine and bromine combine with this substance with great energy, producing crystalline compounds crystallisable from alcohol.

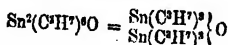
*Zinc-propyl* is formed by acting on mercury-propyl with zinc at  $100^{\circ}-120^{\circ}$ , or by treating propyl iodide with an alloy of zinc and sodium.

*Aluminium-propyl* is produced by acting on mercury-propyl with thin aluminium foil at  $120^{\circ}$  in sealed tubes; it distils in hydrogen at  $240^{\circ}-245^{\circ}$ , and is decomposed by water with production of gelatinous alumina.

*Glucinum-propyl* is formed by acting on mercury-propyl with thin plates of glucinum in a sealed tube at  $130^{\circ}-135^{\circ}$ , and distilling the product in an atmosphere of carbonic anhydride. After rectification it forms a colourless liquid, boiling at  $244^{\circ}-246^{\circ}$ , and in contact with the air, giving off dense fumes which sometimes take fire. At  $-17^{\circ}$  it is a thick oil. Water decomposes it with violence, forming large quantities of gas and glucinum hydrate.

*Stannopropyl Compounds*.—On treating propyl iodide with tin foil or with an alloy of tin and sodium, *stannotripropyl iodide*,  $Sn(C^3H^7)^3I$ , is formed, eight or ten hours

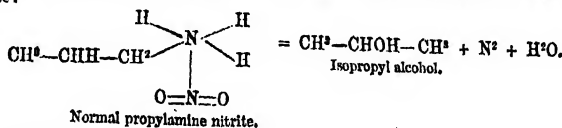
heating in the water-bath in sealed tubes being sufficient. When the contents of the tube are treated with ether, and the ethereal solution of the tin-compound is distilled, a liquid boiling at  $265^{\circ}$ – $272^{\circ}$  passes over, which by rectification easily yields pure stannotripropyl iodide, boiling at  $269^{\circ}$ – $270^{\circ}$ . On heating this substance with strong aqueous potash, *stannotripropyl hydrate*,  $\text{Sn}(\text{C}^3\text{H}^7)_3\text{OH}$ , is obtained as a heavy oil, which concretes on standing to a magnificently crystallised mass made up of inter-laced prisms having an alkaline reaction; this substance is dehydrated by distillation with caustic baryta, forming *stannotripropyl oxide*—



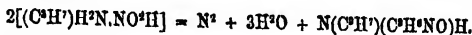
which is reconverted into the hydrate by addition of water; sulphuric acid forms with this oxide a compound but little soluble in water, but crystallisable in fine prisms from alcohol; similarly acetic, formic, butyric acids, &c., form well-crystallised compounds, which much resemble the corresponding substances in the stannotriethyl and stannotrimethyl series.

*Stannotripropyl Cyanide* is obtained as a crystalline sublimate by heating in a tube sealed at one end a mixture of stannotripropyl iodide and silver cyanide.

**Isopropyl Alcohol**,  $\text{CH}^3\text{—CHOH—CH}^3$ . This alcohol may be formed by heating normal propylamine nitrite, prepared by distilling the hydrochloride with silver nitrite:



The crude isopropyl alcohol thus obtained contains nitroso-dipropylamine, formed by the reaction:



This base remains behind when the alcohol, after dehydration with potash, is distilled at the heat of the water-bath.

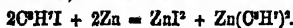
Isopropyl alcohol thus prepared boils at  $82\text{--}85^{\circ}$  (corrected and reduced to 760 mm.) and has a density of 0.7876 at  $16^{\circ}$ .

**Isopropyl Iodide**, prepared from it by the action of hydriodic acid, boils at  $89\text{--}90^{\circ}$  (corrected and reduced). The iodide, bromide, and chloride of isopropyl are easily decomposed by water, and when heated to  $100^{\circ}$  for 48 hours, dissolve in 12.8 and 6 pts. of water, respectively (Linnemann, *Ann. Ch. Pharm.* clxi. 26; *Chem. Soc. J.* [2], x. 236).

**Action of the Copper-zinc Couple on the Iodides of Propyl.**—Isopropyl iodide is rapidly decomposed by zinc alone at its boiling point ( $89^{\circ}$ ), whereas the normal iodide is decomposed very slowly by zinc, even at its higher boiling point ( $101^{\circ}$ ). The iso-compound is decomposed by the copper-zinc couple at about  $50^{\circ}$ , the normal compound at about  $80^{\circ}$ . In this decomposition half of the iso-compound is split up into permanent gases, whereas little, if any, of the normal compound is decomposed in this manner. The resulting liquid in the one case (zinc-isopropyl?) is scarcely volatile; that in the other case (zinc-propyl) rises easily in vapour, notwithstanding its high boiling point. The first is decomposed at about  $132^{\circ}$ , giving mainly gases and metallic zinc; the second distils over unchanged at a higher temperature.

The reaction between the propyl iodide and water, or alcohol, with the couple, takes place much more rapidly in the case of the iso-compound than in that of the normal compound, an olefine making its appearance during the decomposition of the first, but not of the second.

On comparing these results with those obtained with the ethyl and amyl compounds, it is evident that it is the normal, and not the isopropyl iodide that is acted upon in an analogous manner. The main difference perhaps is that there seems to be no crystalline propyl-iodide of zinc, but that the reaction is mainly, if not wholly—



(Gladstone & Tribe, *Chem. Soc. J.* [2], xi. 960).

**Isopropyl Chloride** submitted to the action of chlorine in sunshine in a flask cooled by ice yields two compounds, having the composition  $\text{C}^3\text{H}^7\text{Cl}^2$ , viz. dichloropropane, methyl-dichloroethane or methyl-chloroacetol,  $\text{CH}^3\text{—Cl}^2\text{—CH}^3$ , and propylene dichloride,  $\text{CH}^3\text{—CHCl—CH}^2\text{Cl}$ , the former being the more abundant. The presence

of a trace of iodine facilitates the formation of propylene dichloride at the expense of the dichloropropane, and by the action of iodine chloride in sealed tubes, propylene dichloride only is obtained. Isopropyl bromide is converted by bromine into propylene dibromide (Friedel a. Silva, *Compt. rend.* lxxiii. 1379).

*Isopropyl Benzoate*, formed by the action of a dilute ethereal solution of the iodide on silver benzoate, remains, on evaporating its ethereal solution, as a faintly yellow oily syrup, insoluble in water, and splitting up when heated into benzoic acid and propylene (Linnemann).

*Isopropyl Formate*,  $C^3H^7.CHO^2$ , prepared by the action of isopropyl iodide on cupric acetate at  $120^\circ$ , boils at  $65^\circ-67^\circ$  (bar. at  $44.7$  mm.) The *cyanate*,  $C^3H^7.CNO$ , obtained by treating the iodide with silver cyanate, boils at  $74^\circ$ . *Mono-isopropyl lactate*,  $C^3H^7.C^3H^5(OH)O^2$ , obtained by heating lactic acid with isopropyl alcohol, boils at  $166^\circ-168^\circ$ . *Di-isopropyl lactate*,  $(C^3H^7)^2.C^3H^5O^2$ , formed by the action of isopropyl iodide on the sodium derivative of the preceding ether, boils at a slightly higher temperature (Silva, *Bull. Soc. Chim.* [2], xvii. 97).

*Isopropyl Sulphhydrate*, *Thioisopropyl Alcohol*, or *Isopropyl Mercaptan*, is obtained by mixing isopropyl iodide with an alcoholic solution of potassium sulphhydrate, leaving the mixture to stand for some time in the cold, then slowly heating it on the water-bath till about one-half has distilled over. If the mixture be heated at once, but little mercaptan is obtained, but in place of it a less volatile oil, which, even under the most favourable conditions, constitutes at least a fourth part of the crude product. The above distillate is mixed with water, the oil which separates is dried and rectified, and the portion boiling between  $56^\circ-65^\circ$  is collected apart. By fractional distillation, the main bulk of the mercaptan is obtained, boiling at  $57^\circ-60^\circ$ , but it is impossible to obtain a purer product, since on distillation it is partially decomposed, with evolution of sulphuretted hydrogen.

Thioisopropyl alcohol is violently acted upon by concentrated nitric acid, and converted into isopropyl-sulphonic acid,  $C^3H^7.SO^2OH$ . The potassium salt of this acid is obtained by the action of isopropyl iodide on potassium sulphite. It yields a series of well-crystallised salts (Claus a. Keerl, *Deut. Chem. Ges. Ber.* vi. 659).

**PROPYLAMINES.** On the conversion of normal propylamine into isopropyl alcohol, see p. 1015.

*Tetrapropylammonium Iodide* and *Tetrapropylammonium Hydroxide*.—By digesting normal propyl iodide with alcoholic ammonia, again treating the mixed bases so formed with propyl iodide, distilling off the excess of propyl iodide, and adding soda to a solution of the product, *tetrapropylammonium iodide* is separated in the solid state. It crystallises in beautiful white prisms. By digesting this compound with silver chloride the iodine is replaced by chlorine, and on adding platinum chloride, a red crystalline salt is deposited, having the composition  $[(C^3H^7)^4NCl]PtCl^4$ . When *tetrapropylammonium iodide* is treated with silver hydrate, the hydroxide,  $(C^3H^7)^4N.OH$ , is liberated. It forms a deliquescent mass which absorbs carbonic acid from the air. It is not decomposed at  $100^\circ$ , but at a higher temperature it is decomposed into propylene, tripropylamine, and ammonia.

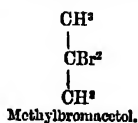
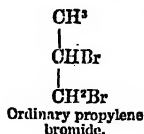
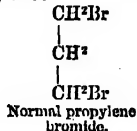
The platinum salt of tripropylamine crystallises in brick-red leaflets, less soluble in water than in alcohol or ether (H. Roemer, *Deut. Chem. Ges. Ber.* vi. 784).

**PROPYLENE** or **PROPENE**,  $C^3H^6=CH^2-CH=CH^2$ . To obtain this hydrocarbon by Berthelot's method of reducing allyl iodide with hydrochloric acid and zinc, Tollens a. Henninger (*Ann. Ch. Pharm.* clvi. 156) gradually pour concentrated hydrochloric acid upon granulated zinc immersed in alcohol of 90 p.c. The gas, which is evolved without application of heat, contains only one-eighth of its volume of hydrogen.

When propylene bromide is treated with sodium amalgam and water, zinc and hydrochloric acid, or zinc and acetic acid, propylene is regenerated in all cases, but when acetic acid is used, the product obtained is sensibly less than with the other reducing agents; there is, moreover, considerable elevation of temperature. On submitting the product to fractional distillation, a viscous mixture of hydrocarbons remains, which is readily attacked by bromine, yielding a mixture of bromides. By fractional distillation this viscous mixture of hydrocarbons yields a mobile liquid boiling between  $70^\circ$  and  $80^\circ$ , as well as one boiling between  $330^\circ$  and  $340^\circ$ . The latter is colourless, slightly viscous, somewhat lighter than water, and appears to consist of hexpropylene,  $(C^3H^6)^2$ ; the liquid boiling between  $70^\circ$  and  $80^\circ$  is probably dipropylene,  $(C^3H^6)$  (Frunier, *Compt. rend.* lxxvi. 98).



**Propylene Bromides,  $C^3H^5Br^2$ .** Three compounds are known, having the composition, viz.:



1. *Ordinary Propylene bromide* is obtained:—1. By the direct union of bromine with propylene. 2. Either pure or mixed with methylbromacetol, by the action of hydrobromic acid saturated at  $10^\circ$  on monobromopropylene. 3. Together with another isomeride boiling at  $163^\circ$ , by the action of hydrobromic acid saturated at  $10^\circ$  on allyl bromide (Géromont, *Bull. Soc. Chim.* [2], xvi. 113; Reboul, *ibid.* xvii. 360). 4. By the action of bromine on isopropyl bromide (Linnemann).

Propylene bromide is a liquid having a sweet taste and smell, a sp. gr. of 1.974, and boiling at  $143^\circ$ . With alcoholic potash it forms bromopropylene boiling at  $51^\circ$ , and the latter treated with sodium alcohol at the temperature of the water-bath yields allylene. (Sawitsch, *Compt. rend.* lii. 399). By silver acetate propylene bromide is converted into propylene diacetate (Wurtz, *Ann. Chim. Phys.* [3], lv. 438), and by silver benzoate into non-crystallisable dibenzoate (Friedel a. Silva, *Compt. rend.* lxxiii. 1370).

A mixture of the bromides of propylene and ethylene in equivalent proportions, such as is obtained when amyl alcohol is decomposed at a red heat and the resulting hydrocarbons are absorbed by bromine, boils constantly at  $134^\circ$ , and cannot be resolved into the constituent bromides by fractional distillation. The separation may, however, be effected by treating the mixture with potassium acetate in alcoholic solution, the ethylene bromide being thereby converted into diacetate, while the propylene bromide remains nearly unaltered (Bauer, *Ann. Ch. Pharm. Suppl.* i. 250).

2. *Normal Propylene bromide*,  $CH^2Br-CHBr-CH^2Br$ ; *Trimethylene bromide* (Géromont); *Hydrobromide of Allyl bromide* (Reboul).—This is the compound which Géromont and Reboul obtained, simultaneously with the preceding, by the action of hydrobromic acid on allyl bromide. It boils at  $162^\circ-164^\circ$ , and has a specific gravity of 2.017 at  $0^\circ$ , 1.93 at  $19^\circ$ . It is decomposed by alcoholic potash at  $100^\circ$ , yielding allyl bromide and allyl-ethyl oxide.

3. *Methyl-bromacetol*,  $CH^3-CBr^2-CH^3$ , *Dichloropropane*, *Dibromethyl-methane*. Formed by the action of pentabromide or trichlorodibromide of phosphorus on acetone, and by direct addition of hydrobromic acid to allylene or its monohydrobromide. It boils at  $115^\circ-118^\circ$  (Linnemann), at  $116^\circ$  (Friedel a. Ladenburg); at  $114^\circ$  (Reboul).

**Bromopropylenes.** 1. *Monobromopropylene*.—Of this compound there appear to be two modifications, isomeric with allyl bromide,  $CH^2=CH-CH^2Br$ .

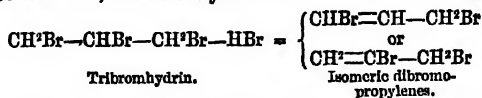
1. Allylene treated with hydrobromic acid yields dibromopropane, or methyl bromacetol, and a bromopropylene having the constitution  $CH^2=CH-CBr=CH^2$ . This latter is also formed by the action of alcoholic soda at  $100^\circ$  on dibromopropane, and by treating the hydrobromide of bromopropylene with alcoholic potash. It boils at  $48^\circ-49^\circ$  under a pressure of 710 mm. and has a specific gravity of 1.39 at  $9^\circ$ . It unites with 2 at. bromine, forming a tribromide which boils at  $190^\circ$ , and is isomeric with bromopropylene bromide boiling at  $194^\circ-196^\circ$ , and with glyceric tribromhydrin boiling at  $217^\circ$ . Monobromopropylene heated to  $100^\circ$  with hydrobromic acid saturated at  $10^\circ$  is reconverted into dibromopropane (Reboul, *Bull. Soc. Chim.* [2], xvi. 60; xvii. 351).

2. Propylene bromide treated with alcoholic potash yields a monobromopropylene which, according to Linnemann (*Ann. Ch. Pharm.* clxi. 43), has a density of 1.4110 at  $15^\circ$  and boils at  $57.6^\circ$  (corr. and reduced); according to Reboul (*Bull. Soc. Chim.* [2], xiv. 60) it boils at  $54^\circ$ , and has a constitution represented by the formula  $CH^3-CH=CHBr$ .

This bromopropylene heated to  $100^\circ$  with mercuric acetate in presence of glacial acetic acid is converted into acetone; by hypochlorous acid and mercuric oxide it is converted into monochloracetone; these reactions do not agree very well with Reboul's formula. The bromopropylene heated to  $100^\circ$  with hydrobromic acid saturated at  $+10^\circ$  forms propylene bromide; but with the same acid diluted with  $\frac{1}{2}$  of its volume of water, it forms, according to a former statement by Reboul (*loc. cit.*), a mixture of methyl-bromacetol and propylene bromide. Bromopropylene unites slowly at common temperatures with concentrated hydriodic acid, forming monobromopropylene hydriodide,  $C^3H^5Br.HI$ . This compound boils with slight decomposition at  $148^\circ$ , and has a density of 2.20 at  $11^\circ$ . It is identical with allylene hydrobromide,  $C^3H^5.HBr.HI$ , and when treated with alcoholic potash yields allylene hydrobromide (b. p.  $48^\circ-49^\circ$ ), together with a small quantity of allylene hydriodide.

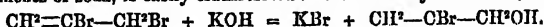
With *hydrochloric acid* of 22° Baumé, bromopropylene yields propylene chlorobromide,  $C^3H^5ClBr$ , boiling at 112°–113°, and having a density of 1.62 at 16° (Reboul). Bromopropylene, heated to 100° in a sealed tube with *sodium ethylate*, yields allylene (Sawitsch, *Compt. rend.* lii. 399).

*Dibromopropylene, Dibromhydroglycide, or Epidibromhydrin*,  $C^3H^2Br_2$ .—This body, of which there are probably two modifications, is formed by the action of potash, or of sodium, on tribromhydrin:



According to Reboul it boils at 151°–152°; according to Henry at about 10° lower; this difference points to the existence of two modifications. It unites with *bromine*, forming  $C^3H^2Br_4$ , and is decomposed by *alcoholic ammonia*, forming dibromallylamine,  $NH(C^3H^2Br)_2$  (ii. 899). With *silver nitrate* in alcoholic solution it forms bromallyl nitrate,  $C^3H^2Br(NO_2)$ , an oily liquid insoluble in water. With *silver acetate* it forms bromallyl acetate,  $C^3H^2Br.C^2H^3O_2$ , a colourless mobile fragrant liquid, insoluble in water, having a density of 1.57 at 12°, boiling at 163°–164°, forming addition-products with chlorine and bromine.

Dibromopropylene, treated with dry *potash* at common temperatures, or distilled with fragments of soda, is easily transformed into bromallyl alcohol,  $C^3H^2BrOH$ :

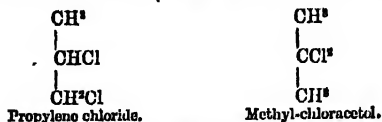


This alcohol, like its acetate, is a colourless, mobile, fragrant liquid, insoluble or slightly soluble in water, having a density of 1.6 at 15°, boiling at 155°. It is attacked by phosphorus pentachloride, giving off hydrogen chloride, and forming monobromallyl chloride,  $C^3H^2BrCl = CH^2=CBBr-CH^2Cl$ . This compound is also a chlorobromopropylene. It boils at 120°, and has a density of 1.63 at 11°. It is probably identical with Reboul's chlorobromhydroglycide or epichlorobromhydrin, formed by heating chlorodibromhydrin with potash (ii. 899).

Monobromallyl alcohol, treated with alcoholic potash, yields propargylic alcohol (p. 1007).

Dibromopropylene, treated with *potassium sulphocyanate* in alcoholic solution, yields bromallyl sulphocyanate,  $C^3H^2Br.CNS$ , which is a colourless pungent liquid boiling at about 200° (L. Henry, *Deut. Chem. Ges. Ber.* v. 186, 452).

**Propylene Chlorides**,  $C^3H^4Cl^2$ . Two bodies having this composition are known, viz.:



*Propylene Chloride* is formed: 1. By the direct action of chlorine on propylene. 2. By passing chlorine into propylene chloriodide under water till all the chlorine is dissolved (this is an easy mode of preparation) (Friedel a. Silva, *Compt. rend.* lxxvi. 1596). 3. By the action of chlorine on propane (Schorlemmer, 1st *Suppl.* 967). 4. Together with methyl-chloracetol, by the action of chlorine in sunshine on isopropyl chloride. 5. By the action of iodine chloride on isopropyl chloride; in this case it is the only compound of formula  $C^3H^4Cl^2$  produced (Friedel a. Silva, *Compt. rend.* lxxiii. 1380).

Propylene chloride is a liquid boiling at 98°, and having a sp. gr. of 1.584 at 0°, 1.165 at 14° (Friedel a. Silva). Treated with alcoholic potash it yields a chloropropylene identical with that which is formed from methyl-chloracetol (Friedel, *Ann. Chim. Phys.* [4], xvi. 349).

*Methyl-chloracetol*,  $CH^3-CH^2-CH^3$ . *Dichloropropane. Dichlorethyl-methane*.—This compound, formed by the action of phosphorus pentachloride on acetone, is a liquid boiling between 25° and 35° (1st *Suppl.* 825). Treated with chlorine or with iodine chloride, it yields a trichlorinated body,  $CH^3-CCl^2-CH^2Cl$ , boiling at 125°, and having a density of 1.350 at 0°, 1.318 at 25°. This trichloride is identical with that which is formed by the addition of chlorine to chloropropylene, and with one of those formed by the chlorination of propylene chloride under the influence of chlorine. It is easily decomposed by water at 175°–180°, yielding a non-volatile product which resinifies when evaporated by heat, reduces ammoniacal silver nitrate, and remains after evaporation in a dry vacuum as a yellow amorphous mass, emitting an odour of caramel when burnt. The residue, insoluble in water, contains two dichloropropylenes.

boiling respectively at  $75^{\circ}$  and  $94^{\circ}$ ; they are formed from methyl-chloracetol by loss of HCl (Friedel a. Silva, *Compt. rend.* lxxiv. 806).

Methyl-chloracetol, heated to  $100^{\circ}$  for several days with silver benzoate in presence of ether, yields crystals of methyl-benzacetol,  $(\text{CH}^3)_2\text{C}=\text{C}(\text{C}^6\text{H}_5\text{O}^2)_2$ , identical with those which Oppenheim obtained in like manner from methyl-chloriodacetol (1st Suppl. 826).

**Dichloromethyl-chloracetol**,  $\text{C}^2\text{H}^4\text{Cl}^4$ , also called *dichloracetone chloride*, is formed by the action of phosphorus pentachloride on dichloracetone. Its properties and reactions have been already described (1st Suppl. 27, 28). Its reduction to allylene by the action of sodium indicates that it is the true tetrachloride of allylene,  $\text{CH}^2=\text{CCl}^2-\text{CHCl}^2$ .

**Methyl-chloriodacetol**,  $\text{CH}^3-\text{CHI}-\text{CH}^2$ , is also described in the 1st Suppl. (p. 826).

**Propylene Chlorobromide**,  $\text{C}^3\text{H}^4\text{BrCl} = \text{CH}^2-\text{CHCl}-\text{CH}^2\text{Br}$ , is obtained by heating propylene bromide with mercuric chloride. It is a liquid boiling at  $120^{\circ}$ , having a sp. gr. of 1.585 at  $0^{\circ}$ , 1.475 at  $18^{\circ}$ . Vapour-density (obs.) = 5.52; (calc.) 5.45. Alcoholic potash converts it into monochloropropylene, boiling at  $25^{\circ}-30^{\circ}$  (Friedel a. Silva, *Bull. Soc. Chim.* [2], xvii. 532).

**Propylene Chloriodide**,  $\text{C}^3\text{H}^4\text{ClI} = \text{CH}^2-\text{CHCl}-\text{CHI}$ . Maxwell Simpson obtained this compound, isomeric with methyl-chloriodacetol, by the action of iodine chloride in aqueous solution on propylene; he describes it as a liquid which cannot be distilled (*ibid.* [2], v. 500). According to Friedel a. Silva (*ibid.* xvii. 535), it is very easily obtained by passing propylene into a bulb-apparatus containing a solution of iodine monochloride, and may be distilled without decomposition. It boils at  $149^{\circ}$  under ordinary pressure, at  $40^{\circ}-43^{\circ}$  under a pressure of 10-12 mm. Sp. gr. = 1.933 at  $0^{\circ}$ , 1.889 at  $25^{\circ}$ . It is limpid, and resembles propylene bromide. It is easily converted into propylene chloride, by heating it to  $100^{\circ}$  with mercuric chloride, or by exposing it to the action of chlorine under water (Friedel a. Silva). Heated with hydriodic acid it is converted into isopropyl iodide (Sorokin, *Deut. Chem. Ges. Ber.* iii. 616).

**Chloropropylenes.** **Monochloropropylene**,  $\text{C}^3\text{H}^4\text{Cl} = \text{CH}^2-\text{CCl}=\text{CH}^2$ , isomeric with allyl chloride,  $\text{CH}^2=\text{CH}-\text{CH}_2\text{Cl}$ , is obtained by the action of potash on propylene chloride, and on methyl-chloracetol; also by the action of silver acetate or of ammonia on methyl-chloracetol. It boils at  $25.5^{\circ}$ , and has a sp. gr. of 0.9307 at  $0^{\circ}$ . Vapour-density = 2.83 (obs.) = 2.65 (calc.) *Sulphuric acid* converts it into acetone (Oppenheim, *Compt. rend.* lxx. 354). It unites with 2 at. bromine, forming the compound  $\text{C}^3\text{H}^4\text{ClBr}_2 = \text{CH}^2-\text{CClBr}-\text{CH}^2\text{Br}$ , which boils at  $170^{\circ}-175^{\circ}$ , and has a sp. gr. of 2.064 at  $0^{\circ}$ . This chlorobromide, treated with *alcoholic potash* or *silver acetate*, gives up HBr, and is converted into a chlorobromopropylene,  $\text{C}^3\text{H}^4\text{ClBr} = \text{CH}^2-\text{CCl}=\text{CHBr}$ , or  $\text{CH}^2=\text{CCl}-\text{CH}^2\text{Br}$ , which boils between  $100^{\circ}$  and  $110^{\circ}$  (Friedel, *Ann. Chim. Phys.* [4], xvi. 343). It is isomeric with Reboul's chlorbrom-hydroglycide,  $\text{CH}^2-\text{CBr}=\text{CH}^2\text{Cl}$ .

Chloropropylene, heated to  $120^{\circ}$  with *alcoholic potash*, is converted into allylene (Friedel, *Compt. rend.* lix. 294). It combines with *hydrogen iodide* at  $100^{\circ}$ , forming methyl-chloriodacetol. *Chlorine* in sunshine converts it into  $\text{C}^3\text{H}^4\text{Cl}^2$ , isomeric with glyceric chlorhydrin, boiling at  $127^{\circ}$ , and identical with dichloromethyl-chloracetol.

**Dichloropropylenes**,  $\text{C}^3\text{H}^4\text{Cl}^2$  (Friedel a. Silva, *Compt. rend.* lxxiii. 957; lxxiv. 806; lxxv. 81).—Three of these compounds are known, namely:



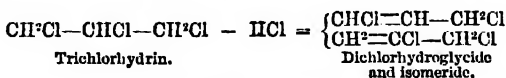
The first two are formed simultaneously when monochloropropylene is treated with chlorine in the shade. The first boils at  $75^{\circ}$ , the second at  $94^{\circ}$ ; the latter, which forms by far the larger part of the product, is identical with the dichloropropylene which is produced, together with dichlorhydroglycide (boiling at  $108^{\circ}$ ), by the action of dry potash on trichlorhydrin. The third compound is dichlorhydroglycide.

1. The dichloropropylene melting at  $75^{\circ}$  is likewise obtained by the action of water at  $180^{\circ}$  and of alcoholic potash on dichloromethylchloracetol. It unites with bromine less readily than the following compound, forming a bromide which boils with partial decomposition at  $190^{\circ}$ .

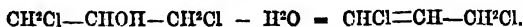
2. The dichloropropylene boiling at  $94^{\circ}$ ,  $\text{CH}^2=\text{CCl}-\text{CH}^2\text{Cl}$ , is formed in both the reactions above mentioned, especially in the first; also in that of dry potash on tri-

chlorhydrin. It combines energetically with bromine, forming a very stable bromide which boils at 205°; easily also with hydrochloric acid when heated with a solution saturated at 6°, forming dichloromethylchloracetol. Sulphuric acid converts it into monochloracetone (Henry, *Deut. Chem. Ges. Ber.* v. 86). With alcoholic potash it yields a chlorinated ether,  $\text{CH}^2=\text{CCl}-\text{CH}^2.\text{OC}^2\text{H}^5$ , boiling at 110°, having a density of 1.011 at 0°, and 0.995 at 21°. This ether takes up 2 at. bromine, forming a chlorobrominated ether,  $\text{CH}^2\text{Br}-\text{CClBr}-\text{CH}^2.\text{OC}^2\text{H}^5$ .

3. *Dichlorhydroglycide* or *Epidichlorhydrin*,  $\text{CHCl}=\text{CH}-\text{CH}^2\text{Cl}$  (b.p. 106°), is formed, together with the second isomeride, by the action of potash on trichlorhydrin:



It is obtained pure by the action of phosphoric anhydride on dichlorhydrin (b.p. 174°):



Allyl-alcohol dichloride,  $\text{CH}^2\text{Cl}-\text{CHCl}-\text{CH}^2\text{OH}$ , which is isomeric with dichlorhydrin, does not yield it. It does not unite with hydrochloric acid. With alcoholic potash it likewise yields a chlorinated ether,  $\text{CHCl}=\text{CH}-\text{CH}^2.\text{OC}^2\text{H}^5$ , boiling at 120°-125°, and having a density of 1.021 at 0° and 0.991 at 25°. This ether appears to be identical with that which Henry obtained by addition of  $\text{Cl}^2$  to ethyl-allyl oxide, and treatment of the product with alcoholic potash. It takes up 2 at. bromine, forming a product which distills at about 220°, but decomposes at the same time, with separation of easily alterable, uncrystalline, crystalline laminae (Friedel u. Silva).

Isomeric with the three dichloropropylones is the chloride obtained from acrolein by the action of phosphorus pentachloride (i. 147). Its constitution, which results directly from that of acrolein, is represented by the formula,  $\text{CH}^2=\text{CH}-\text{CHCl}^2$ .

*Tetrachloroglycide*,  $\text{C}^2\text{H}^2\text{Cl}^4$ , formed by fixation of chlorine on dichlorhydroglycide, is a colourless liquid having a strong ethereal odour, density = 1.406 at 17°, and boiling at 164°. The isomeric compound, dichloracetone dichloride, formed by the action of phosphorus pentachloride on acetone (1st Suppl. 27), boils at 153°.

Sodium acts strongly on tetrachloroglycide, but if this compound be diluted with hydrocarbons and slowly heated, gas is evolved with regularity, consisting of allylene mixed with propylene.

Tetrachloroglycide treated with alcoholic potash yields a chloride,  $\text{C}^2\text{H}^2\text{Cl}^2$ , boiling at 142° and having a density of 1.414 at 20°.

Alcoholic ammonia transforms tetrachloroglycide into tetrachlorodiallylamine,  $\text{NH}(\text{C}^2\text{H}^2\text{Cl}^2)^2$ , which is a colourless alkaline liquid, decomposing at 200°, slightly soluble in water, soluble in acids. Its *hydrochloride* forms white needles soluble in water and in alcohol. The *platinochloride*,  $2[\text{NH}(\text{C}^2\text{H}^2\text{Cl}^2)^2.\text{HCl}].\text{PtCl}_4$ , crystallises in small crimson prisms, soluble in water and in alcohol, less soluble in ether. The *sulphate* is uncrystallisable. The *dioxalate*,  $\text{NH}(\text{C}^2\text{H}^2\text{Cl}^2)^2.\text{C}^2\text{H}^2\text{O}^4$ , is very soluble in water and crystallises from alcohol in leaflets (Pfeffer u. Fittig, *Ann. Ch. Pharm.* cxxxv. 357).

*Chlorobromoglycide* or *Epichlorobromhydrin*,  $\text{C}^2\text{H}^2\text{ClBr} = \text{CHCl}=\text{CH}-\text{CH}^2\text{Br}$  or  $\text{CHBr}-\text{CH}=\text{CH}^2\text{Cl}$ , obtained by the action of dry potash on chlorodibromhydrin, has been already described (i. 899). It boils at 126°-127°, and is isomeric with the chlorobromopropylene,  $\text{CH}^2=\text{CCl}=\text{CHBr}$  or  $\text{CH}^2=\text{CCl}-\text{CH}^2\text{Br}$ , obtained by abstraction of  $\text{HBr}$  from the chlorobromide of propylene (p. 1019).

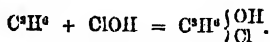
*Trichloropropylene*,  $\text{C}^2\text{H}^2\text{Cl}^3$ .—Obtained, together with dichlorallylene, by decomposing crotonic chloral with caustic soda. It is a liquid of agreeable odour, boiling between 138° and 140°. It has not, however, been obtained pure. It is not attacked by soda-ley in the cold, but alcoholic potash quickly removes from it a molecule of hydrogen chloride, converting it into dichlorallylene. Trichloropropylene takes up 2 at. bromine (Pinner, *Deut. Chem. Ges. Ber.* v. 206).

**Propylene Glycols, Propylene Hydroxides, or Propylene Alcohols**,  $\text{C}^2\text{H}^4(\text{OH})^2$ . Two of these compounds are known, viz.:—1. *Ordinary Propylene glycol* or *Propyl-glycol*,  $\text{CH}^2-\text{CHOH}-\text{CH}^2\text{OH}$ , analogous to ordinary propylene bromide, and obtained by saponifying the corresponding propylene diacetate with potash (Wurtz). This compound has been already described as *TRIPYLENE GLYCOL* (v. 882).

2. *Normal Propylene Glycol*,  $\text{CH}^2\text{OH}-\text{CH}^2-\text{CH}^2\text{OH}$ . *Trimethylene glycol*.—This compound, probably analogous to malonic acid,  $\text{GO}^2\text{H}-\text{CH}^2-\text{CO}^2\text{H}$ , is prepared by treating normal propylene bromide (p. 1017) with silver acetate in presence of

acetic acid, and saponifying the resulting diacetate (b. p. 203°–205°) with baryta. It is a thick saccharine liquid boiling between 206° and 218° (Géromont, *Deut. Chem. Ges. Ber.* iv. 548; Reboul, *Bull. Soc. Chim.* [2], xvii. 350).

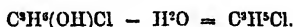
**Propylene Chlorhydrin** or **Monochlorhydrin of Propyl-glycol** (ordinary),  $C^3H^5 \begin{smallmatrix} OH \\ | \\ Cl \end{smallmatrix} = CH^2-CH.OH-CH^2Cl$ . Produced by the action of gaseous hydrogen chloride on propylene glycol; the mixture at first becomes hot, but must be warmed on the water-bath towards the end to complete the reaction. The product is distilled up to 135°, and then treated with sodium carbonate to neutralise the hydrochloric acid. Two layers of liquid are thus formed, the upper of which consists of the chlorhydrin. The greater part distils over at 127°. The same compound is obtained by the action of hypochlorous acid on propylene:



Propylenic chlorhydrin boils at 127°. Sp. gr. = 1.302 at 0°. Vapour-density = 3.38 (obs.) = 3.26 (calc.) It is neutral, has an ethereal odour and a saccharine but pungent taste. It dissolves in water, also in alcohol, ether, and a mixture of the two, but is insoluble in solutions of sodium chloride and calcium chloride. Sodium carbonate does not act on it at ordinary temperatures, but when heated converts it into propylene oxide. Aqueous potash immediately decomposes it into potassium chloride and propylene oxide (Oser, *Bull. Soc. Chim.* 1860, 235).

Propylenic chlorhydrin, heated with *potassium cyanide* in sealed tubes, is converted into the corresponding cyanhydrin,  $C^3H^5(OH)CN$ , which when boiled with *potash* yields  $\beta$ -oxybutyric acid,  $CH^3-CHOH-CH^2-CO^2H$  (1st *Suppl.* 891).

*Phosphoric anhydride* converts propylenic chlorhydrin into a mixture of allyl chloride and monochloropropylene:



Propylenic chlorhydrin unites with *bromine* in sunshine, without evolution of hydrobromic acid (Henry a. Henninger, *Deut. Chem. Ges. Ber.* iv. 602).

**Propylene Nitrate**, or **Propylenic Dinitrin**,  $C^3H^5(NO^2)^2 = CH^2-CH(NO^2)-CH(NO^2)$ . Fuming nitric acid acts violently on nitric acid, rendering it necessary to cool the mixture during the reaction. On subsequently adding water, propylene nitrate is deposited as a colourless oil (Henry, *loc. cit.*)

**Propylene Oxide**,  $C^3H^5O = CH^2-CH-CH^2$ . This compound is obtained, by adding aqueous potash to crude propylene chlorhydrin, as a very volatile liquid which may be purified by fractional distillation. It must be dried with fused potash, as calcium chloride retains it. It is a neutral liquid, having an ethereal odour, and a harsh pungent taste. Boils at 35°. Sp. gr. = 0.859 at 0°. Vapour-density = 2.0 (obs. and calc.) It is miscible in all proportions with water, alcohol and ether, insoluble in solution of calcium or magnesium chloride. Heated for a few seconds in a sealed tube with magnesium chloride, it forms a copious precipitate of magnesium hydrate (Oser, *Bull. Soc. Chim.* 1860, 237).

Epichlorhydrin,  $C^3H^5ClO$ , is the oxide of chloropropylene.

**Propylene Benzoate**,  $C^3H^5(C^7H^5O^2)^2$ . A. Mayer described this compound as forming fine crystals isomorphous with ethylene benzoate (1st *Suppl.* 300); but according to Friedel a. Silva (*Compt. rend.* lxxiii. 1379), it is a viscid uncrystallisable liquid, boiling at 240°, under a pressure 12–14 mm.

The *acetate*, *cyanide*, *iodide*, *sulphide* and *sulphocarbonate* of propylene are described, in vol. v. p. 893, as **TRITYLENIC ETHERS**.

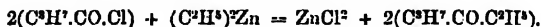
**PROPYLENE-DIAMINE**,  $C^3H^5(NH^2)^2$ , (Hofmann, *Deut. Chem. Ges. Ber.* vi. 308). This base is obtained by heating propylene bromide with ammonia in a closed vessel. On heating the product with potash in the water-bath, to expel ammonia and alcohol, and then raising the temperature, propylene-diamine passes over at about 120°. At higher temperatures, 200° and above, viscous bases distil over, probably consisting of secondary and tertiary diamines. To dehydrate the propylene-diamine, it is heated with sodium, then distilled in a stream of hydrogen, and again heated with sodium.

Anhydrous propylene-diamine is a colourless, transparent, mobile liquid, boiling at 119°–120°, and having a density of 0.878 at 15°. It is so hygroscopic, that a glass rod moistened with it fumes in the air; it also rapidly attracts carbon dioxide. The *hydrate*,  $2C^3H^5.NH^2.H^2O$ , boils at the same temperature as the anhydrous base. The

*hydrochloride*,  $C^3H^4(NH^2)^2 \cdot 2HCl$ , forms long white needles, very hygroscopic, and very freely soluble in water, less soluble in alcohol.

The *platino-chloride*, formed only in concentrated solution, crystallises in beautiful four-sided plates. The *hydrobromide* and *hydriodide* greatly resemble the hydrochloride; has not been obtained in crystals.

**PROPYL-ETHYL KETONE**,  $C^3H^{12}O = C^3H^7 \cdot CO \cdot C^2H^5$ . *Ethyl-butyryl*.—This compound, isomeric with Frankland & Duppa's isobutyl-methyl-acetone and with methyl-valeryl, was discovered by Friedel amongst the products of the distillation of calcium butyrate (i. 608), and is produced synthetically by the action of zinc-ethyl on butyryl chloride (Butlerow, *Bull. Soc. Chim.* [2], v. 17):



It is a liquid boiling at  $122^\circ$ – $125^\circ$ , having a density of 0.818 at  $17.5^\circ$ . It does not unite with sodium bisulphite at ordinary temperatures, but on heating the mixture, and then leaving it to cool, crystalline scales are deposited which ultimately dissolve. In the dry state the combination is stable, but water quickly resolves it into propyl-ethyl ketone and sodium bisulphite.

The ketone oxidised by potassium dichromate and dilute sulphuric acid is converted into propionic acid:  $C^3H^7 \cdot CO \cdot C^2H^5 + O^2 = 2(C^2H^5O \cdot OH)$ , (Popoff, *Ann. Ch. Pharm.* clxi. 285).

**PROPYL-METHYL CARBINOL**,  $C^3H^7 \cdot CHOH \cdot CH^3$  (see AMYL ALCOHOLS, 1st Suppl. 111).

**PROPYL-METHYL KETONE**,  $C^3H^{10}O = C^3H^7 \cdot CO \cdot CH^3$ . This ketone was also first noticed by Friedel, amongst the distillation-products of calcium butyrate; Butlerow obtained it synthetically by the action of zinc-methyl on butyryl chloride; and it has been especially studied by Friedel (*Ann. Chim. Phys.* [4], xvi. 366), and by Grimm (*Ann. Ch. Pharm.* clvii. 249), both of whom obtained it by the distillation of a mixture of acetate and butyrate of calcium. Schorlemmer (p. 63) has obtained it by oxidation of the secondary alcohol derived from normal pentane. It is a colourless liquid, boiling at  $111^\circ$  (Friedel), at  $102^\circ$ – $105^\circ$  (Schorlemmer), at  $99^\circ$ – $101^\circ$  (Grimm), at  $95^\circ$  (Butlerow), and having a density of 0.837 at  $0^\circ$ , 0.8078 at  $15^\circ$  (Grimm). It is only slightly soluble in water, but mixes freely with alcohol and ether. It unites with alkaline bisulphites, forming crystallisable compounds which are decomposed by water. The sodium salt contains  $C^3H^7NaSO^3 + 1\frac{1}{2}H^2O$ .

The ketone treated with phosphorus pentachloride reacts like ketones in general, exchanging O for  $Cl^2$ , and forming methyl-chlorobutyrol, or dichloropentane,  $C^3H^7Cl^2$ , which boils at about  $140^\circ$ , and is resolved by distillation into hydrogen chloride and chloramylene or chloropentane,  $C^3H^5Cl$ , boiling at about  $95^\circ$ . This last body, heated to  $140^\circ$  with alcoholic potash, again gives up  $HCl$ , and is converted into valerylene,  $C^4H^6$ , a homologue of acetylene, which distils towards  $50^\circ$  (v. 981), (Friedel).

Propyl-methyl ketone combines directly with nascent hydrogen, forming propyl-methyl carbinol,  $C^3H^{10}O = C^3H^7 \cdot CHOH \cdot CH^3$  (1st Suppl. 111), (Grimm), and a pinacone,  $C^6H^{12}O^2$ , which boils at  $225^\circ$ – $230^\circ$ , and when recently distilled, forms a colourless liquid, but solidifies after some time to a white crystalline mass, melting at a gentle heat (Friedel).

Propyl-methyl ketone yields, by oxidation with chromic acid mixture, acetic and propionic acids, with a small quantity of carbonic acid (Schorlemmer).

Propyl-methyl ketone is identical with the ethyl-acetone of Frankland & Duppa, and isomeric with propiono, isopropyl-methyl ketone (1st Suppl. 768), and valeral.

**PROPYL-PHYCITE**,  $C^3H^4(HO)^4$ ? (1st Suppl. 963). Experiments apparently confirming the existence of this supposed compound have been made by J. G. Wolff, in Carius's laboratory (*Ann. Ch. Pharm.* cl. 28); but Carius himself has thrown doubt upon their accuracy (*Bull. Soc. Chim.* [2], xiv. 240), and further experiments by Claus (*Deut. Chem. Ges. Ber.* iii. 525) tend to corroborate his former conclusion that the supposed propyl-phycite does not exist.

**PROTEIDS.** Several attempts to get an insight into the molecular construction of these bodies have lately been made, but with only very partial success. The most important are, perhaps, Nasse's experiments, from which he has drawn some conclusions as to the state in which their nitrogen exists in them, (*Studien über die Eiweisskörper*; *Pflüger's Archiv.* vi. p. 589); he treated various proteids in the dried and powdered state with caustic baryta for forty or fifty hours, and systematically

examined the products of decomposition; the main result at which he arrives is that, in the same proteid, nitrogen exists in several very different states of combination, part being held very firmly, and part being easily turned out. From the comparison of the combinations in which the loosely-held nitrogen appears, with the results of the action of caustic baryta on nitrogenous bodies whose molecular constitution is known, such as amine-acids, acid amides, nitrides, leucine, &c., he considers it extremely probable that a definite quantity of the loosely-combined nitrogen of proteids is combined as in amides; another part as the nitrogen in creatine or the more loosely-held portion of the nitrogen of uric acid, and most of the remainder as in the acid amides and the difficultly expulsi- ble nitrogen of creatine or sarcosine.

Béchamp (*Compt. rend.* 1870) oxidised proteids with potassic permanganate, and found that urea was produced, together with many other bodies; as almost all proteids taken into the body leave it in the form of urea, this result promised to be of importance, but very great doubt has been thrown upon its accuracy (Loew, *J. pr. Chem.* 1870). Treated with powerful oxidising bodies, proteids yield various acids of the fatty series, and their aldehydes, benzoic acid, ammonia, and various compound ammonias.

The complete separation of proteids from animal fluids has been much facilitated by a new method of precipitation devised by Brücke (*Wien. Akad. Ber.* 1871); this consists in acidulating the liquid with hydrochloric acid, and then adding to it a solution of potassio-mercuric iodide, made by saturating with mercuric iodide a boiling solution of potassic iodide.

The changes which proteids undergo in the animal body from the time they enter it from the alimentary canal until they leave it as urea, or uric acid, are still almost totally unknown. It has already been pointed out (GLYCOGEN, p. 567) that there is considerable reason to believe that they are partly broken up in the liver, bile-acids and urea being produced from them, together with glycogen; while in the muscles (MUSCULAR TISSUE, p. 830) it would appear that much less breaking up of proteids occurs than was formerly supposed (see also UREA). In the alimentary canal the gastric juice splits them up into peptones, parapeptones and other bodies, and one of the pancreatic ferments also converts them into peptones, but afterwards goes further, and breaks the peptones up into tyrosine and leucine (see DIASTASE, p. 430). Peptones do not appear to exist either in the blood or in chyle, and so must be converted into some other form of proteid immediately upon entering either of these fluids.

H. N. M.

**PROTocatechuic Acid,  $C^H^O^4$ .** This acid has been shown by Barth (*Deut. Chem. Ges. Ber.* iv. 633), and Romsen (*Zeitschr. f. Chem.* vii. 81, 199, 294), to be the 1 : 3 : 4 form of dioxibenzoic acid,  $C^H^3$   $\begin{matrix} OH \\ OH \\ COOH \end{matrix}$  (p. 431).

It is formed from piperonylic acid (methylene-protocatechuic acid) by heating the latter to 150° with dilute hydrochloric acid, the only products of the reaction being protocatechuic acid and free carbon:



With pure water at 210° the same decomposition takes place, but the protocatechuic acid is resolved by the high temperature into  $CO^2$  and pyrocatechin (Fittig & Romsen, *Ann. Ch. Pharm.* clix. 129). Conversely piperonylic acid may be formed synthetically by heating protocatechuic acid with methylene iodide and potassium hydrate (p. 983).

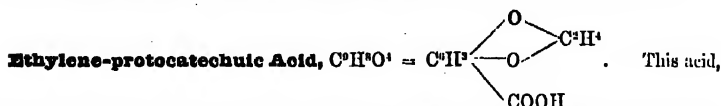
**Preparation from Kino.**—Stenhouse finds that East Indian kino is the best source of protocatechuic acid, and the one which yields it most readily. One part of the kino in fine powder is gradually added to three parts of fused sodic hydrate, stirring the mixture constantly during the introduction of the kino, the most convenient method being to sift the fine powder over the surface of the hydrate, which is kept fused at a gentle heat. When the mixture has acquired a bright orange-brown colour, it is poured out on a stone or an iron plate, and allowed to cool. The cake is then broken up and dissolved in about 20 pts. of hot water, to which dilute sulphuric acid is added from time to time, so as to render the solution slightly acid. The dark brown solution is then allowed to stand for 24 hours, when it deposits a large quantity of sodium sulphate in the crystalline state; the mother-liquors which contain the protocatechuic acid, after being filtered to remove a small quantity of tarry matter, are agitated with ether. The ethereal solution is then separated, and the ether recovered by distillation in the water-bath; the dark-coloured syrupy residue on standing deposits the protocatechuic acid in the crystalline state. The mother-liquors may be

readily separated from the crystals by means of the vacuum pump, and the acid is then easily purified by one or two crystallisations from a small quantity of hot water, with the addition of some freshly precipitated lead sulphide, which removes the brown colouring matter (*Chem. Soc. J.* [2], xiii. 8).

**Action of Bromine.**—Barth has shown that protocatechuic acid treated with excess of bromine in the cold is converted into bromopyrocatechuic acid,  $C^6H^3BrO^4$ , by simple substitution of Br for H (1st *Suppl.* 976). If, however, this monobrominated acid, or pyrocatechuic acid itself, be heated in sealed tubes with excess of bromine to  $100^\circ$ , a totally different reaction takes place, resulting in the formation of tetrabromopyrocatechin (Stenhouse, *loc. cit.*):



On Dimethyl- and Diethyl-protocatechuic acids, see pp. 431, 432 of this volume.



homologous with piperonylic acid (methylene-catechuic acid) is formed similarly to the latter (p. 983), by mixing 3.5 grams of protocatechuic acid, in a tube, with 10 grams of ethylene bromide and 4½ grams of solid potassium hydrate, then sealing the tube, and shaking it, with occasional immersion in warm water, till the free protocatechuic acid and the potash have united into a brown viscid mass; this treatment is absolutely necessary to the success of the experiment. The tube is then heated in the water-bath for five or six hours and shaken from time to time; the mass afterwards exhausted with hot alcohol; the solution gently warmed with potassium hydrate, and the residue mixed with water and dilute hydrochloric acid, and well shaken with ether. On evaporating the ether, the ethylene-protocatechuic acid remains as a dark-coloured mass, which may be easily purified by recrystallisation from water, with addition of animal charcoal.

Ethylene-protocatechuic acid crystallises from water in colourless indistinct crystals, from alcohol in druses of short shining prisms. It closely resembles piperonylic acid, and, like the latter, is nearly insoluble in water, but in boiling water it dissolves much more readily than piperonylic acid. It melts at  $133^\circ$ , and at a higher temperature sublimes without decomposition in shining prisms. Its calcium salt crystallises well, and is somewhat sparingly soluble. The barium salt crystallises in large, finely developed transparent crystals, which apparently belong to the orthorhombic system. The solutions of these salts give a yellow precipitate with ferric chloride (Fittig a. Remsen, *Zeitschr. f. Chem.* vii. 289).

**PROTocatechuic ALDEHYDE**,  $C^6H^4O^3 = C^6H^3 \begin{Bmatrix} (OH)^2 \\ CHO \end{Bmatrix}$ . This compound is formed, with separation of carbon, by heating piperonal (methylene-protocatechuic aldehyde) with dilute hydrochloric acid, just as protocatechuic acid is formed from piperonylic acid; also, together with hydrochloric acid and carbon dioxide, by heating dichloropiperonal with water (Fittig a. Remsen, *loc. cit.*) For its properties and reactions, see 1st *Suppl.* 976.

**PROTOPINE**,  $C^6H^5NO^3$  (Hesse, *Zeitschr. f. Chem.* vii. 653). An alkaloid occurring in very small quantity in opium, and obtained from the mother-liquors remaining after the separation of morphine by the Robertson-Gregory process. The method of separating it from the other bases present in these mother-liquors is given in the article *Opium Bases* (pp. 876-877). The protopine is finally precipitated from the solution of its hydrochloride by ammonia, and dissolved in acetic acid; the solution is treated with a small quantity of charcoal, and, after addition of alcohol, precipitated by ammonia.

Protopine is a white crystalline powder, insoluble in water, slightly soluble at the boiling heat in alcohol, benzene and acetone, almost insoluble in the last two liquids at common temperatures. Chloroform dissolves it also, but moderately, though more readily than other solvents. Ether dissolves it very sparingly; when recently precipitated it dissolves in ether somewhat more freely, but separates partially after a short time in warts or spherical groups of prisms, which are very characteristic of protopine, as no other alkaloid of opium forms crystals of similar character. Cryptopine under the same circumstances separates in rhombohedrons.

Protopine is slightly soluble in caustic potash and soda; it does not colour ferric chloride. With strong nitric acid it forms a colourless solution, which turns yellow on



the slightest warming. Pure concentrated nitric acid forms at 20° a yellow solution which after some time turns red, and finally bluish-red; acid containing ferric oxide forms immediately a dark violet solution; at 150° both solutions change to dirty brownish-green.

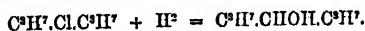
Protopine melts at 262° with partial decomposition; it has an alkaline reaction, and neutralises acids; the salts have a bitter taste, and do not gelatinise.

The *hydrochloride* forms rather large, apparently rhombic prisms, very sparingly soluble in hot and in cold water. The *platinochloride*,  $2(C^{20}H^{23}NO^3.HCl).PtCl_4 + 2H_2O$ , is a yellow crystalline precipitate, slightly soluble in cold water. The *bitartrate* forms small prisms, somewhat sparingly soluble in cold water. The *bioxalate* forms warty groups of prisms which dissolve easily in boiling water, with difficulty in cold water, though more readily than the corresponding cryptopine salt. The *sulphate* forms small needles.

**PSEUDO-ACONITINE**, syn. with NAFELLINE; also called ACRACONITINE. See ACONITE ALKALOIDS (p. 23).

**PSEUDOCORALLIN**. This name is applied by H. Fresenius to Wanklyn's Caro's rosolic acid (1st Suppl. 999; also p. 391 of this volume).

**PSEUDOHEPTYL ALCOHOL**. *Dipropyl Carbinol*.—Obtained, together with butyrene-pinacone, by the action of sodium on dipropyl ketone (butyrene) mixed with a little water:



It boils at 149°–150° (Schorlemmer's normal heptyl alcohol from petroleum boils at 175.5°–177.5°), dissolves sparingly in water, easily in alcohol in all proportions. By oxidation with potassium dichromate and sulphuric acid, it is converted into butyrene. With iodine and phosphorus, it yields the corresponding *iodide*,  $C^8H^{17}.CHI.C^8H^{17}$ , which has a density of 1.2 at 20°, and boils with partial decomposition at 180° (C. M. Kurz, *Ann. Ch. Pharm.* clxi. 205).

**PSEUDOISOPYRINE**. See ISOPTRYNE (p. 707).

**PSEUDOMORPHINE**,  $C^{17}H^{19}NO^4$ . Hesse (*Zeitschr. f. Chem.* [2], vii. 643). Many kinds of opium appear to contain little or none of this base. For the method of separating it from the other opium-bases see 1st Suppl. 976. On mixing the hot dilute aqueous solution of its hydrochloride with potassium-sodic tartrate, a hydrate of pseudomorphine separates in white shining scales, having nearly the composition  $C^{17}H^{19}NO^4 + 4H_2O$ ; the same solution precipitated with ammonia, gives scales whose composition is nearly  $C^{17}H^{19}NO^4 + 1\frac{1}{2}H_2O$ . Hesse supposes that there are two hydrates containing respectively 1 and 4 mols. of water, and that the precipitates above mentioned are mixtures of the two.

Pseudomorphine dissolves in strong *sulphuric acid*, without colour at first, but the solution soon turns olive-green, and if slightly heated, quickly assumes a dingy green colour. Water added to a solution recently prepared in the cold throws down crystalline pseudomorphine sulphate. With *nitric acid* of sp. gr. 1.06°, pseudomorphine forms in the first instance a nitrate of pseudomorphine; but if the nitric acid is in excess, a nitrate of nitropseudomorphine, separating in small yellow crystals, which, however, very quickly decompose. Pseudomorphine is not altered by sulphurous acid, by hydrogen sulphide, or by zinc, either in acid or in alkaline solution.

*Acid Tartrate of Pseudomorphine*,  $C^{17}H^{19}NO^4.C^4H^5O^6 + 6H_2O$ , may be prepared by adding tartaric acid to the solution of the acetate; it crystallises in small prisms, which dissolve in 429 pts. of water at 18°, and are moderately soluble in boiling water. The *hydrobromide*, formed on adding potassium bromide to a solution of the acetate, crystallises in small prisms, slightly soluble in water. The *hydriodide*,  $C^{17}H^{19}NO^4.HI + H_2O$ , is formed by adding potassium iodide to a solution of the hydrochloride, slightly acidulated with acetic acid; it crystallises in small prisms, soluble in 793 pts. of water at 18°. The *chromate*,  $2C^{17}H^{19}NO^4.Cr^2H^2O^7 + 4H_2O$ , separates on adding potassium dichromate to the aqueous solution of the hydrochloride, in small yellow prisms, which appear brownish-yellow in the mass, coffee-brown after drying at 80°. It gives off two-thirds of its water of crystallisation over sulphuric acid, the remainder at 80°; takes fire when heated a little above 100°. Dissolves in 990 pts. water at 18°; insoluble in alcohol.

**PSEUDOPURPUREIN**. See PURPUREIN.

**PSEUDOTOLUIC ACID**. See TOLUIC ACID.

**PSEUDOTOLUIDINE**. See TOLUIDINE.

2nd Sup.

3 U.

**PUCHERITE.** This mineral is a bismuth vanadate found in a mine at Schneeberg in Saxony, in small crystals of the rhombic system, mostly recognisable only with the lens. The following combinations have been observed:—

1.  $\infty P . oP$ , and  $oP . \infty P$ .
2.  $\infty P . \tilde{P}\infty$ .
3.  $\infty P . oP . m\tilde{P}n$ .
4.  $oP . \infty P . \tilde{P}\infty . m\tilde{P}n$ , and  $\infty P . \tilde{P}\infty . m\tilde{P}n . oP$ .

A pyramid of the principal series  $mP$ , and the pinacoids  $\infty \tilde{P}\infty$ , and  $\infty \tilde{P}\infty$ , have also been observed, the two latter, however, only in very narrow strips. Twins likewise occur.

Cleavage perfect parallel to the base. Lustro vitreous to adamantine. Colour reddish-brown to brownish-red; occasionally also limpid yellowish-brown, hyacinth-red, and dark yellowish-brown. Streak-powder, ochre-yellow. Opaque to translucent. Hardness near that of fluorspar. Sp. gr. (allowing for adhering quartz) = 6.249.

The mineral decrepitates violently before the blowpipe; melts on charcoal, and gives a yellow deposit of bismuth oxide, and when fused on charcoal with sodium carbonate, yields metallic bismuth. With borax and phosphorus salt, it gives the reactions of vanadium.

It dissolves easily in hydrochloric acid, with evolution of chlorine, forming a deep red liquid, which becomes green on standing, or immediately on dilution with water; when poured into a large quantity of water, it yields a yellowish-white precipitate of basic bismuth chloride containing vanadic acid; with ammonia it yields a yellowish to greyish-white precipitate of vanadiferous bismuth hydrate.

Analysis gave 73.16 p.c.  $Bi^2O^3$ , 22.19  $V^2O^3$ , 3.66  $As^2O^3$ , 1.34  $P^2O^5$  (= 100.35), agreeing with the formula of a bismuth monovanadate,  $Bi^2O^3.V^2O^3$ , in which the vanadium is partly replaced by arsenic and phosphorus (Frenzel, *J. pr. Chem.* [2], iv. 227, 361; *Jahrb. f. Mineralogie*, 1872, 514). On the crystalline form, see also Welsky (*ibid.* 1873, 183).

**PURPLE OF CASSIUS.** See GOLD (p. 576).

**PURPURATES and ISOPURPURATES** (E. Kopp, *Deut. Chem. Ges. Ber.* 7, 644). The best yield of potassium isopurpurate is obtained by mixing intimately finely powdered picric acid with twice its weight of potassium cyanide and a little water. After half an hour more water is added, and the mixture is heated to  $40^\circ$ – $45^\circ$ , and then allowed to cool; the crystals separating out are pressed and purified according to Hlasiwetz's method (iii. 434).

In dyeing with isopurpurates the same mordants are used as in dyeing with murexid, the best being mercury and lead salts. Murexid produces on mercury mordant a splendid purple with a violet tint, while isopurpurates dye purple having a brownish-orange tint; the colours produced by the latter are neither acted upon by sunlight nor by sulphurous acid, which quickly destroys murexid. On silk mordanted with zinc, murexid gives a fine yellow, and isopurpurates a dark, reddish-brown. Murexid colours are destroyed by acids and alkalis, whilst those of the isopurpurates assume only a yellowish tint.

Purpurates are not explosive. On adding hydrochloric acid to a somewhat concentrated solution it becomes colourless, and after some time dialuramide crystallises out. Nitric acid oxidises them to alloxan, and when caustic soda-solution is added to a solution of a purpurate, the solution becomes first bluish-violet, and on standing, or more quickly on heating, colourless.

Isopurpurates explode on heating, some very violently; on adding hydrochloric acid to a solution it becomes yellowish-brown and opaque, and afterwards brown amorphous flakes separate out. Nitric acid changes their colour to orange, and caustic soda in the cold to brownish-violet, whilst on heating, ammonia is given off, and the colour is changed to a dark, yellowish-brown. Isopurpurates are also decomposed by ammonia, but more slowly than by the fixed alkalis. Hydrogen sulphide reduces ammonium isopurpurates, sulphur separating out, while the liquid becomes yellowish-red, and assumes a dirty colour when exposed to the air. The products of decomposition of isopurpuric acid are still colouring matters, dyeing silk like the aniline-browns called Vesuvian and Bismarck.

**PURPURINO-COBALT SALTS.** See COBALT (p. 366).

**PURPURIN.** The following characteristics of this and other colouring matters of madder are given by Schützenberger (*Dingl. pol. J.* cxvii. 438).

*Characters of Madder-dyes.*

	Alizarin	Purpurin	Pseudopurpurin	Orange Dye	Purpuroxanthin
Absorption-bands in Spectrum	Near the Red	Near Red and in Yellow		None	None
Crystallisation	Orange needles	Red needles	Brick-red needles	From alcohol in small lumps	Yellow needles
Sublimation	Easy	Decomposed in great part		Decomposes, yielding purpurin	—
Solution in Alkalies	Purple-blue	Red	Red	Red	Yellow
Solubility in Benzine	Soluble	Soluble	Soluble	Insoluble	Soluble
Solubility in Alcohol	More soluble in hot than in cold	More soluble in hot than in cold	Very slightly soluble even in hot alcohol	Easily soluble	Soluble

The behaviour of these colouring matters in dyeing is as follows: *Alizarin* yields permanent dyes, red-violet and violet, which withstand the action of nitromuriatic acid and of soap. *Purpurin* and the *orange dye* give fast colours which withstand soap and nitromuriatic acid tolerably well; bright-red or greyish-violet. *Pseudo-purpurin* gives brick-red or pale violet colours, destroyed by soap and nitromuriatic acid. *Purpuroxanthin* gives less pure colours, orange-yellow with alumina mordants, pale grey with iron mordants.

**PYRENE**,  $C^{10}H^{10} = C^{10}H^8(C^2H^2)$ . *Phenylene-naphthalene* (Graebe, *Ann. Chem. Pharm.* clviii. 285).—A hydrocarbon occurring, together with chrysene (p. 338), in the last portions of the distillate obtained in distilling coal-tar down to coke.\* The two bodies are separated by means of carbon sulphide, which dissolves the pyrene and leaves the chrysene. The carbon sulphide having been distilled off, the residue is exhausted with warm alcohol, and the cooled filtered solution is mixed with a cold alcoholic solution of picric acid as long as a red crystalline precipitate of pyrene picrate is produced. This precipitate is collected on a filter, washed with alcohol, decomposed by heating with ammonia, and the hydrocarbon thereby separated is washed with water and recrystallised from alcohol till it melts at  $142^{\circ}$ – $144^{\circ}$ , to bring it to which point it must, in some cases, be reconverted into the picrate.

Pyrene crystallises from hot alcohol, in which it is somewhat freely soluble, in leaflets resembling those of anthracene. It often retains a yellowish colour, which may be removed by exposing its solution in benzene to sunshine. It is very soluble in benzene, ether, and carbon sulphide, and separates from benzene or ether, or by slow crystallisation from alcohol, in rather large rhombic plates. It melts at  $142^{\circ}$ , sublimes with difficulty in small plates, and distils at a temperature considerably above  $360^{\circ}$ . With very dilute *nitric acid* it forms only nitro-derivatives, no acid. With chromic acid it yields a quinone. *Hydriodic acid* converts it into hydrocarbons analogous to the hydrides of anthracene. With *bromine* it forms both substitution- and addition-products; with sulphuric acid, sulpho-acids.

*Pyrene Picrate*,  $C^{10}H^{10}.C^2H^2(NO^2)_2OH$ , crystallises from ether, benzene, hot alcohol, and other solvents, in long, red, shining needles, very slightly soluble in cold alcohol, somewhat abundantly in carbon sulphide and ether, very easily in benzene. It is slowly decomposed by hot water, quickly by alkalis.

*Nitropyrenes*.—*Mononitropyrene*,  $C^{10}H^8(NO^2)$ , is formed when pyrene is heated for two hours with a mixture of equal volumes of nitric acid, of sp. gr. 1.2, and water; and melts to a reddish oil which solidifies on cooling. By recrystallisation from hot alcohol, it is obtained in yellow needles, melting at  $140^{\circ}$ – $142^{\circ}$ , slightly soluble in cold alcohol, somewhat more soluble in hot alcohol, easily in ether and in benzene. *Dinitropyrene*,  $C^{10}H^6(NO^2)_2$ , is obtained by boiling pyrene with nitric acid of sp. gr. 1.45, extracting the mononitropyrene formed at the same time by boiling with alcohol, and finally crystallising from glacial acetic acid. It forms slender yellow needles, slightly soluble in alcohol, ether, and benzene. *Tetranitropyrene*,  $C^{10}H^4(NO^2)_4$ , is formed when

\* The substance described as pyrene by Laurent (l. v. 754) was doubtless a mixture of hydrocarbons containing a considerable proportion of pyrene.

dinitropyrene is boiled for a long time with nitric acid of sp. gr. 1.5, and crystallises in lustrous needles from glacial acetic acid, in which it is slightly soluble. It is almost insoluble in alcohol, and very slightly soluble in ether and in benzene. It melts at about 300°.

**Bromopyrenes.**—*Dibromopyrene Dibromide*,  $C^{16}H^8Br^2$ , is formed when finely pulverised pyrene is exposed for a day under a bell-jar to the action of bromine vapour, the bromine being kept constantly in excess. The product, crystallised from nitrobenzene, forms faintly-yellow needles soluble in aniline and nitrobenzene, nearly insoluble in alcohol, ether, and benzene.

*Tribromopyrene*,  $C^{16}H^8Br^3$ , separates in the solid state on adding a slight excess of bromine to a solution of pyrene in carbon sulphide, hydrobromic acid being evolved at the same time. It crystallises from nitrobenzene in colourless needles, which may be freed from the solvent by washing with ether. It is almost insoluble in alcohol, ether, and carbon sulphide, somewhat more soluble in benzene, easily soluble in hot nitrobenzene and aniline.

**Pyrene-quinone**,  $C^{16}H^8O^2$ .—When solid chromic acid is added to a hot solution of pyrene in glacial acetic acid, a strong reaction takes place, resulting in the formation of pyrene-quinone, the greater part of which separates during the reaction, the rest on addition of water. After washing with water, and recrystallisation from glacial acetic acid, it forms red needles or prisms. On adding water to the acetic acid solution, the quinone is precipitated as a brick-red powder very slightly soluble in alcohol, ether, benzene, and carbon sulphide, very easily in nitrobenzene. It dissolves in strong sulphuric acid, with a brown colour, and when heated with zinc-dust is reconverted into pyrene.

*Hexhydropyrene*,  $C^{16}H^{14}$ .—Pyrene is not acted on by sodium-amalgam. Heated to 200° with hydriodic acid (b.p. 127°) in presence of amorphous phosphorus, it is converted into a mixture of hydrides, from which the hexhydride may be isolated by repeated crystallisation from alcohol. It melts at 127°, does not combine with picric acid in alcoholic solution, and when passed through a red-hot tube is reconverted into pyrene.

**PYRIDINE.** This base is found, together with several of its homologues, in tobacco-smoke (see TOBACCO).

It is formed when the hydrochlorides of certain monomorphine derivatives are heated with potash (p. 825).

Ethylene-platinochloride of pyridene,  $2(C^5H^2N.HCl).PtCl^4$ , crystallises in rhombohedrons (V. v. Lang, *Chem. Centr.* 1872, 535).

**PYRITES, CAPILLARY.** See NICKEL SULPHIDES (p. 851).

**PYRITES.** On the Estimation of Sulphur in Pyrites, see SULPHUR.

**PYROCATECHIN**,  $C^6H^4O^2 = C^6H^3(OH)^2$ . This modification of dioxybenzene has hitherto been generally regarded as belonging to the meta-series or isophthalic series, 1 : 3 (p. 137); but recent investigations have rendered it more probable that it is an ortho-compound, 1 : 2 (see PHENOLS, p. 924).

Pyrocatechin has been found in living plants, e.g. in the green leaves of the Virginia Creeper (*Ampelopsis heteracea*) (Gorup-Besanoz, *Deut. Chem. Ges. Ber.* iv. 905).

Flückiger (*ibid.* v. 1) is of opinion that pyrocatechin is contained in the sap of the plants from which kino is prepared, and that it is not formed during the preparation of the kino—which consists simply in boiling down the sap—since the temperature at which this operation takes place cannot greatly exceed 100°. The residues from the ethereal extract of kino-gums from various sources gave, when dissolved in water, the characteristic pyrocatechin reaction, viz., a grass-green coloration on addition of ferric chloride, changed to red by lime-water.

**Formation from Cellulose.**—Hoppe-Seyler (*Deut. Chem. Ges. Ber.* iv. 15) observes that pyrocatechin is produced, together with carbon dioxide and formic acid, when paper (Swedish filter-) is heated with water to 200° for four to six hours. Paper heated to 210° in a stream of carbon dioxide gives off, as already observed by Pettenkofer, a little water and traces of formic acid, but no pyrocatechin. Starch, cane-sugar, and milk-sugar, heated with water to 280°, are carbonised, and give off comparatively larger quantities of carbon dioxide with less pyrocatechin.

When pyrocatechin is heated with *phthalic anhydride*, and water is added to the mixture, a greenish liquid is formed which exhibits, with potash, a very transient blue colour (Bayer, *Deut. Chem. Ges. Ber.* iv. 663).

**Action of Bromine and Water on Bromopyrocatechin.**—When tetrabromopyrocatechin is treated with bromine and water, a substance (provisionally called *oxybromopyrocatechin*) is formed, consisting of dark crimson plates, which melt at 138° and are soluble in benzene and in carbon tetrachloride. Its composition is represented by

the empirical formula,  $C^{10}H^7Br^{10}O$ , and it appears to be formed in the manner shown by the equation:



An ethereal solution of erythroprocatechin, treated with aqueous sodium carbonate, yields a sodium compound analogous to the corresponding derivative of xanthogallol (*q.v.*) It has a deep green colour, and brilliant metallic lustre, and decomposes readily when left in contact with alkaline solutions (Stenhouse, *Chem. Soc. J.* [2], xii. 586; xiii. 6).

#### PYROCHLOR. See TANTALATES.

**PYROGALLOL** or **PYROGALLIC ACID**,  $C^6H^3O^3 = C^6H^2(OH)^1$ . *Reaction with Iron Salts.*—Pyrogallol produces, in a solution of pure ferrous sulphate, a white milky precipitate which disappears on exposure to the air, the liquid turning blue. The presence of a ferric salt is therefore required to obtain the characteristic blue colour with pyrogallol, but the quantity must be small. Thus, on using a mixture containing oven 2 pts. of ferric salt to 100 of ferrous sulphate, the blue colour changed in a few minutes into red. The red solution of pyrogallol and a ferric salt deposits, on standing, a precipitate consisting first of pure purpuragallin; then a mixture of this body and tanuo-melanate of iron is obtained, and at last only the latter compound is formed.

When ammonia is gradually added to a dilute solution of ferric chloride and pyrogallol, the red solution first becomes blue and then bright red. On adding acetic acid the blue colour is restored, but changed into a greenish tint by an excess of the acid; and on addition of ammonia the liquid again becomes blue and then red. Hydrochloric acid also destroys the blue colour, the original red being reproduced. By means of this reaction the presence of 1 pt. of a ferric salt in 100,000 of water can be easily detected, and even on using only 1 c.c. containing 0.00005 gram, the liquid acquires a distinct amethyst tint. When pyrogallol is added to a solution of ferric chloride and potassium ferrieyanide containing a slight excess of the latter, a blue precipitate is formed which is soluble in water. Ammonia changes this colour into an amethyst-red, and acetic acid again into blue. When pyrogallol is added to ferric acetate or a mixture of a ferric salt and an organic salt of the alkali-metals or metals of the alkaline earths, a beautiful purplish-blue solution is obtained, which is coloured a fine red by alkalis. Organic acids restore the blue colour, while inorganic acids turn the liquid reddish-brown. The blue liquid is also formed by using ammonium succinate, gum-arabic or its compound with lime, or an alkaline solution of albumin, but not by the compounds of lime with the sugars, or by ferric acetate which has been prepared from ferric sulphate and lead acetate, and heated for some hours on a water-bath; (this solution is also without action on potassium ferrocyanide. The reaction of ammonia with pyrogallo-ferric chloride is so delicate, that by means of it 1 gram of ferric chloride will impart a purple-red colour to 2 hectolitres of water. When the blue solution is boiled, a bluish-black precipitate, insoluble in alcohol, is formed, and a similar change takes place slowly at the common temperature. A solution of pyrogallo-ferric chloride may sometimes be used in place of litmus. Thus, while red litmus is not changed by aniline, an acid solution of pyrogallo-ferric chloride assumes a beautiful blue colour on addition of aniline (Jacquemin, *Compt. rend.* lxxvii. 593; lxxviii. 1155).

*Pyrogallate of Lead.*—Stenhouse prepared this salt by dropping a solution of neutral lead acetate into an excess of pyrogallol, and assigned to it the composition,  $3PbO.4C^6H^3O^3$  or  $2C^6H^3O^3.PbO^2.PbH^2O^2.H^2O$  (i. 759)\*. W. H. Doering, however, finds that the precipitate thus formed is a double salt of pyrogallate and acetate of lead, that the composition of which is the same as that  $C^{12}H^6PbO^6.(C^6H^3O^3)^2Pb$ , the percentage composition of which is the same as that required by Stenhouse's formula. When gently warmed with alcohol and sulphuric acid, it gives off acetic ether, in quantity very nearly equal to that which should be produced from a salt having the composition just stated. It is possible that many insoluble lead salts of organic acids prepared by precipitation from lead acetate, and said to be basic salts containing *m* molecules of lead salt + *n*PbO, may really be double salts containing lead acetate (*Chem. Soc. J.* [2], xi. 702).

*Oxidation of Pyrogallol.*—*a. By Electrolysis.*—Pyrogallol is easily oxidised by electrolysis. At first, the oxygen eliminated at the positive pole is entirely absorbed; afterwards carbon dioxide is evolved in large quantity, and ultimately a mixture of this gas with oxygen and carbon monoxide.

*B. By Active Oxygen.*—H. Struve (*Ann. Ch. Pharm.* clxiii. 160) finds that pyrogallol undergoes slow oxidation when its aqueous solution is mixed with lead dioxide, gum arabic, extract of malt, grape-juice, colouring matter of blood, or saliva, and exposed

\* There printed erroneously  $C^{12}H^6PbO^6.PbH^2O^2$ .

to the air. In presence of either of these substances, a dilute solution of pyrogallol gradually assumes a wine-yellow, or even a darker colour, and deposits small yellow capillary needles of purpurogallin (*1st Suppl.* 977), the solution remaining clear throughout. Cane-sugar, grape-sugar, starch, pepsin, and urine do not act in this way.

The easiest way of setting up this reaction is to mix 50 c.c. of a 1 p.c. solution of gum arabic\* with 0.2 p.c. pyrogallol. The pyrogallol dissolves almost immediately, and the separation of purpurogallin begins after a few hours. A solution of purpurogallin is coloured deep blue by alkalis, as previously observed by Girard, and the reaction may serve for the detection even of very small quantities of this body. If, however, the purpurogallin is still contaminated with traces of pyrogallol or with other products of decomposition, it is coloured more or less brownish by alkalis. Purpurogallin, like pyrogallol, gives Trommer's reaction with cupric sulphate and an alkali.

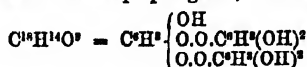
As gum reacts with pyrogallol in a similar manner to blood, Struve infers that it discharges in plants a function similar to that of blood in the animal organism—that is to say, it acts as a carrier of oxygen.

When ozonised oil of turpentine is shaken up with pyrogallol, purpurogallin is formed, and dissolved by the turpentine. On agitating this oil with water, and a few drops of ammonia, the water acquires a transient blue colour.

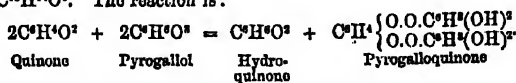
Struve adduces experiments which demonstrate the incorrectness of Schönbein's statement (*Jahresb. f. Chem.* 1860, 55), that hydrogen dioxide can exist in contact with pyrogallol, and that during the oxidation of a solution of pyrogallol mixed with caustic soda, hydrogen dioxide is formed in the liquid. Struve further observes that, when solutions of pyrogallol in pure water, or in water containing potash or gum, are exposed in large glass flasks to the action of the air, best in sunshine, and strips of ozone-paper are suspended in the flasks, a very distinct ozone reaction becomes manifest in a few hours.

According to J. D. Boeke (*Deut. Chem. Ges. Ber.* vi. 486; *Chem. Soc. J.* [2], xi. 1031), pyrogallol dissolved in aqueous potash (1 mol. pyrogallol to 3 mols. potassium hydrate), and exposed to the action of ozonised air, is converted into an acid having the composition  $C^6H^4O^7$ .

*γ. By Chromic Acid.*—According to Wichelhaus (*ibid.* v. 846) pyrogallol is converted by oxidation with chromic acid into a product difficultly soluble in chloroform and benzene, and crystallisable with some difficulty from alcohol. Wichelhaus regards this product as identical with Girard's purpurogallin, but assigns to it the formula:



*Reaction with Quinone.*—Pyrogallol dissolves quinone, forming pyrogalloquinone,  $C^6H^4O^8$ . The reaction is:



Pyrogalloquinone is a red crystalline substance, which does not melt below  $200^\circ$ , and may be sublimed, but not without considerable loss. It is decomposed by alkalis, yielding blue solutions which soon turn black (Wichelhaus, *loc. cit.*)

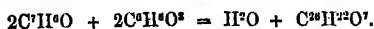
*Reactions with Aldehydes.*—When pyrogallol is dissolved in aqueous *methylens acetate*, not in excess, and fuming hydrochloric acid is added—whereby formaldehyde is produced (p. 533)—the liquid quickly solidifies, from separation of a body which is soluble in water but insoluble in hydrochloric acid, and precipitates gelatin. If formaldehyde is present in excess, the precipitate, which is at first white, immediately turns red, forming a very permanent dye-stuff. The amorphous, colourless body boiled with dilute hydrochloric or sulphuric acid yields small, colourless needles, which appear to be insoluble in water. If the boiling be continued too long, the liquid and the crystalline compound become dark-coloured. An analysis of the compound gave 68.18 p.c. carbon and 4.66 hydrogen (Baeyer, *Deut. Chem. Ges. Ber.* v. 1096).

*Acetaldehyde-ammonia* dissolved in hydrochloric acid gives, on addition of strong hydrochloric acid, a white precipitate consisting of a greasy substance easily soluble in water. On heating a mixture of aldehyde, hydrochloric acid, and pyrogallol, a red substance is produced. Chloral reacts with pyrogallol like aldehyde (Baeyer, *ibid.* 26).

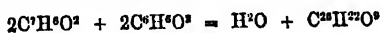
\* Gum which has been treated with hydrochloric acid is indifferent towards pyrogallol; but it does not become inactive by purification with acetic acid, or by the boiling of its solution.

On mixing *furfural* with pyrogallol and moistening with a trace of hydrochloric acid, an indigo-blue substance is formed, which dissolves in water with green colour and is precipitated by hydrochloric acid in blue flocks (Bayer, *ibid.* 25).

*Benzaldehyde* heated with pyrogallol yields, as chief product, a colourless, resinous compound,  $C^{26}H^{22}O^7$ , which crystallises from solution in ether. At the same time, there is formed a red oxidation-product which dyes calico like gallein, but bluer, and is converted by reducing agents into the colourless body just mentioned. This substance, heated to  $200^\circ$ , gives off hydrogen, and is converted into a red compound,  $C^{26}H^{20}O^7$ , which dissolves with dark red colour in alcohol. The colourless body is immediately obtained pure by mixing a cold solution of pyrogallol in hydrochloric acid with a well-shaken mixture of benzaldehyde and a very large quantity of hydrochloric acid. The clear solution becomes turbid in a few seconds, and deposits the substance in question in the perfectly colourless state. On heating the mass with hydrochloric acid, part of it turns red, while another portion is converted into the crystalline compound. The latter is at once obtained perfectly pure by adding highly concentrated hydrochloric acid by small portions to a boiling solution of pyrogallol and benzaldehyde in a large quantity of absolute alcohol, till the crystalline precipitate which forms after a while no longer alters. The whole is then to be quickly cooled, left to itself for a day, and the precipitate washed with alcohol. The body thus obtained is perfectly colourless, almost insoluble in alcohol, slightly soluble in acetone, crystallises in obliquely truncated prisms, and has the same composition as the resinous body formed in the cold, viz.,  $C^{26}H^{22}O^7$ , its formation being represented by the equation:

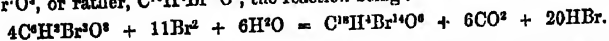


If, in the last experiment, *salicyl*ol be used instead of benzaldehyde, a similar reaction takes place. Only a small quantity of alcohol must, however, be used, since the resulting compound is easily soluble therein. This compound is colourless, crystallises in six-sided tables, and has the composition  $C^{26}H^{22}O^8$ , its formation being represented by the equation:



(Bayer, *ibid.* 280).

*Action of Bromine, in presence of Water, on Tribromopyrogallol* (Stenhouse, *Chem. Soc. J.* [2], xii. 586; xiii. 1).—When tribromopyrogallol is added to about twice its weight of bromine and then 5 to 10 pts. of water are poured on the mixture, there is a slight development of heat, and both the bromine and the bromopyrogallol dissolve, forming a deep orange-coloured solution. If this be heated to  $70^\circ$ - $80^\circ$ , it begins to effervesce from evolution of carbonic anhydride, and a substance is gradually deposited in bright yellow crystalline plates which have a composition represented by the formula,  $C^4H^2Br^2O^3$ , or rather,  $C^4H^4Br^4O^6$ , the reaction being:



After purification by crystallisation from carbon sulphide and light petroleum, it forms brilliant yellow plates which melt at  $122^\circ$ , and are very soluble in ether, benzene, and carbon sulphide. It is also soluble in alcohol, but undergoes decomposition at the same time. This substance, called provisionally *Xanthogallol* (*q. v.*), is better prepared by the action of bromine and water on pyrogallol itself.

If, instead of treating the bromopyrogallol with twice its weight of bromine, only one part be added, the whole dissolves as before on addition of water, forming an orange-coloured solution. On allowing this to stand for a short time at the ordinary temperature, colourless scales begin to separate, and gradually increase until the mixture, if sufficiently concentrated, becomes semi-solid. The substance thus formed is somewhat soluble in water, and decomposes when gently heated. It does not appear to be converted into the yellow compound when treated with excess of bromine.

**PYRIGOALLOQUINONE.** See the last article.

**PYROMELLITIC ANHYDRIDE.** On the action of this compound upon naphthol, and the composition of the resulting naphtholic pyromelliteins, see p. 840.

**PYROMORPHITE.** The following are recent analyses of this mineral: 1, 2, 3, from Chester Co., Pennsylvania; 1, dark olive-green; 2, yellowish-green; 3, somewhat darker than 2 (Williams, *Chem. News*, xxi. 84):

	$3PbO.P^2O^5$	$3CaO.P^2O^5$	$3FeO.P^2O^5$	$PbCl^2$	$CaF^2$	Insol.
1.	87.40	0.37	1.74	9.79	0.84	0.42 = 100.00
2.	85.89	2.64	0.62	9.41	0.67	trace = 99.23
3.	87.01	trace	1.39	9.13	0.91	trace = 98.14

These specimens contained a small quantity of silver, estimated at 0.0037 p.c.  
4. From Shapbach, in the Schwarzwald, containing traces of fluorine and of cupria

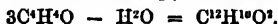
oxide, to the latter of which the beautiful apple-green colour of the mineral is evidently due. Sp. gr. = 6.416 at 20°.

	P <sup>2</sup> O <sup>5</sup>	As <sup>2</sup> O <sup>5</sup>	PbO	CaO	Pb	Cl
4.	16.25	0.61	68.60	3.28	7.95	2.62 = 99.31

(Petersen, *Jahrbuch f. Mineralogie*, 1871, 393).

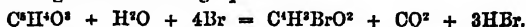
Specimens of pyromorphite from Cumberland have been found to contain didymium, the quantity of which, judging from the intensity of the absorption-bands, is about equal to that in asparagus stone (C. Horne, *Chem. News*, xxvi. 109).

**PYROMUCIC ACID**, C<sup>4</sup>H<sup>4</sup>O<sup>8</sup> (Limpricht, *Ann. Chem. Pharm.* clxv. 278). This acid is produced in small quantity only by the dry distillation of mucic acid, and is best obtained by the action of alcoholic potash on furfural. By distilling it with phosphorus pentachloride a mixture of different bodies is formed which could not be separated. When the barium salt mixed with soda-lime is heated, a compound called tetraphenol, C<sup>4</sup>H<sup>4</sup>O<sup>4</sup>, distils over. It is a colourless liquid, having a peculiar smell, and boiling at 32°. Tetraphenol is not acted upon by alkalis, and its alcoholic solution is not precipitated by lead or silver salts. Sodium and potassium have no action upon it, nor is it changed by passing carbon dioxide into its ethereal solution containing sodium, or by heating it with sodium and carbon dioxide in a closed tube. It does not combine with the bisulphites of the alkali-metals, and remains unaltered when sodium-amalgam is added to its alcoholic solution. Acids act readily on it; concentrated hydrochloric decomposes it with the greatest violence, and dilute acids more slowly, with formation of the so-called pyrrol-red:



When 2 mols. of bromine are added to a solution of 1 mol. of pyromucic acid, carbon dioxide is evolved, and a very small quantity of an oily liquid separates out. By shaking the aqueous solution with ether, evaporating the ethereal solution on a water-bath, and drying the residue over sulphuric acid, a yellowish syrup is left behind, from which, on standing, white warty crystals, having the composition C<sup>4</sup>H<sup>4</sup>O<sup>8</sup>, separate out. This body has an acid reaction, and its solution is coloured yellow by excess of alkali. When baryta-water is added until the liquid has only a faint acid reaction, alcohol produces a white precipitate having the composition (C<sup>4</sup>H<sup>4</sup>O<sup>8</sup>)<sub>2</sub>·Ba. An excess of baryta-water produces a yellowish precipitate, the quantity of which increases on heating the solution, which has the same composition. The compound, C<sup>4</sup>H<sup>4</sup>O<sup>8</sup>, is also formed by the action of lead oxide or potassium dichromate and dilute sulphuric acid on pyromucic acid; by acting with sodium-amalgam on its aqueous solution, the bodies C<sup>4</sup>H<sup>4</sup>O<sup>8</sup> and C<sup>4</sup>H<sup>4</sup>O<sup>8</sup> were formed, and bromine oxidises it to fumaric acid, which appears to be also formed by boiling it with water and silver oxide. It seems probable therefore that the compound C<sup>4</sup>H<sup>4</sup>O<sup>8</sup> is the aldehyde of fumaric acid, although it does not combine with the bisulphites of the alkali-metals.

The compound C<sup>4</sup>H<sup>4</sup>O<sup>8</sup> is not always formed by the action of 2 mols. of bromine on pyromucic acid and water, but several times the body C<sup>4</sup>H<sup>4</sup>BrO<sup>8</sup> was produced, which is formed according to the following equation:



This compound forms white feathery crystals melting at 84°, and smelling like camphor. It readily volatilises with the vapour of water, and is soluble in ether and alcohol, but not in water. Alcoholic potash does not act on it at 180°. By adding sodium-amalgam and sulphuric acid to an alcoholic solution, the compound C<sup>4</sup>H<sup>4</sup>O<sup>8</sup> is formed, a heavy very refractive liquid, smelling like benzene, which is not acted on by hydrochloric acid and alkalis, and does not combine with alkaline bisulphites.

When an excess of bromine is added to pyromucic acid in presence of water, mucobromic acid, C<sup>4</sup>H<sup>4</sup>Br<sup>2</sup>O<sup>8</sup> (p. 828), is formed:



**Isopyromucic Acid**, C<sup>4</sup>H<sup>4</sup>O<sup>8</sup>, is produced, together with pyromucic acid, a small quantity of an empyreumatic oil, formic acid, water, carbon dioxide, carbon monoxide, and a gas burning with a luminous flame, by the dry distillation of mucic acid. The operation must be performed in a retort, of which only one-sixth is filled, and heat is applied, first very slowly, so that only one drop passes over every two minutes; afterwards the retort is gradually heated to a dull red-heat. It takes about eight hours to decompose 30 grams of mucic acid. Isopyromucic acid decomposes carbonates but slowly, and may therefore easily be separated from the other acids by digesting the distillate with barium carbonate, and shaking the solution with ether. It is readily soluble in water, and sublimes slowly at 100° in a current of carbon dioxide, in small plates softening at 70°, and becoming perfectly liquid at 82°. It is a monobasic acid.



Its aqueous solution is coloured brown by alkalis; baryta-water in excess produces a bulky precipitate, and, on boiling, the solution acquires a deep-red colour. On adding bromine to the aqueous solution of the acid, a crystalline body insoluble in water is formed, together with mucobromic acid (Limpriecht).

Stenhouse (*Chem. News*, xxiv. 303) describes another isomeric acid of pyromucic acid, distinguished as  $\beta$ -pyromucic acid, the silver salt of which he obtained by digesting fucosol (ii. 918) at  $100^\circ$  with recently precipitated silver oxide and water. The acid separated from this salt by precipitating the silver with hydrochloric acid, and evaporating the solution at  $100^\circ$ , is a brown semi-crystalline mass, from which petroleum-ether extracts the acid, leaving the colouring matter undissolved. The acid thus separated may be purified by one or more crystallisations from boiling water. It crystallises from aqueous solution in rhombic plates melting at  $130^\circ$ , whereas ordinary pyromucic acid, prepared from furfural, crystallises in smooth needles, and melts at  $133^\circ$ . Silver  $\beta$ -pyromucate,  $C^3H^3AgO^3$ , is moderately soluble in boiling water, and separates, on cooling, in long flat needles.

**PYROPHOSPHATES.** On the formation of these salts by the decomposition of hypophosphites, see p. 966.

**PYROPHOSPHORIC SULPHOBROMIDE**,  $P^2S^2Br^4$ . See PHOSPHORUS COMPOUNDS (p. 963).

**PYRORACEMIC** or **PYRUVIC ACID**,  $C^3H^3O^3$ . *Action of Phosphorus Pentachloride.*—When 4 or 5 pts. of the pentachloride are gradually added to 1 pt. of pyroracemic acid, the mixture being ultimately warmed till all the pentachloride is dissolved, the cooled liquid treated with alcohol till hydrochloric acid ceases to escape, and then mixed with a large quantity of water, a red-brown oil separates, which, after washing with water, and drying with calcium chloride, distils at  $160^\circ$ , yielding ethyl dichloropropionate,  $C^2H^2Cl^2O^2.C^2H^2$ , as a colourless liquid having a specific gravity of 1.2493 at  $0^\circ$ . Dilute aqueous ammonia converts this ether into a white crystalline mass melting at  $116^\circ$ , and having the composition  $C^2H^2Cl^2NO$  (Klimenko, *Deut. Chem. Ges. Ber.* iii. 465).

Böttiger (*ibid.* vi. 893), by adding phosphorus pentachloride to pyroracemic acid cooled by a freezing mixture, treating the product with alcohol, and subsequently distilling, obtained a distillate of ethyl acetate, and a residue from which water separated ethyl dichloropropionate.

When pyroracemic acid is heated with water to  $130^\circ$ , a small quantity of carbonic anhydride is evolved, probably due to the formation of a trace of pyrotartaric acid, but the bulk of the pyroracemic acid remains unchanged. When, however, the heat is raised to  $160^\circ$ , a considerable quantity of carbonic anhydride is evolved, and products not yet investigated are formed (Böttiger, *ibid.* vi. 787). With baryta-water pyroracemic acid yields acetic and oxalic acids, besides urtic acid,  $C^4H^4O^4$  (v. 971) (Böttiger, *loc. cit.*)

Barium peroxide acts violently on pyroracemic acid, forming the barium salt of an acid containing  $C^3H^3O^3$ , probably formed according to the equation  $3C^3H^3O^3 - H^2O = C^3H^3O^3$ . When pyroracemic acid is heated with strong nitric acid, oxalic acid is formed, together with small quantities of formic and carbonic acids (Böttiger, *ibid.* vi. 790).

When pyroracemic acid, partly neutralised with baryta, is heated with water to  $130^\circ$  for several hours, an acid,  $C^3H^3O^4$ , containing 2 at. hydrogen more than urtic acid, is obtained in shining crystals melting at  $133^\circ$  and volatilising completely when heated on platinum-foil (Böttiger, *ibid.* 893).

Wislicenus, by acting on 1 mol. pyroracemic acid with 2 at. bromine, obtained a crystalline acid,  $C^3H^3Br^2O^3$ , which was transformed into lactic acid by nascent hydrogen and was therefore probably dibromolactic acid (iv. 770). According to P. de Clermont (*Bull. Soc. Chim.* [2], xix. 103) this acid, when acted upon in the fused state by chlorine, evolves hydrochloric acid, and yields a product which crystallises from its aqueous solution in large, flat, rhombic crystals, efflorescent in the air and in a vacuum, and melting at about  $93^\circ$ . This product is free from chlorine, but contains bromine, and, notwithstanding discrepancies in analysis, De Clermont believes it to be identical with the dibromopyruvic acid of Wichelhaus,  $(C^3H^3Br^2O^3)$ , with which it agrees in properties:



Pyroracemic acid, heated to  $100^\circ$  for some time with hydrochloric acid in a sealed tube, undergoes decomposition, carbon dioxide being formed in abundance. The liquid yields, on evaporation, crystals having the composition of pyrotartaric acid, and melting at  $110^\circ$ – $112^\circ$  (De Clermont).

Sulphopyrroacemic acid, heated to  $100^{\circ}$  with aqueous solution of bromine in a sealed tube, yields a syrupy, non-crystallisable, brominated acid. Sulphopyrroacemate of barium, submitted to the same treatment, yields bromosulphopyrroacemate of barium, crystallisable, and soluble in water (De Clermont).

**Pyroacemic Ethers.**—Pyroacemic acid does not yield an ether by treatment with alcohol and hydrochloric or sulphuric acid; neither is the ethylic ether obtained by acting on the silver salt with ethyl iodide diluted with dry ether, the only results of the reaction being free pyroacemic acid and condensation-products. Methyl iodide, on the other hand, yields a pyroacemic ether when similarly treated, but even in this case much of the acid is liberated.

**Methyl pyrroacemate**,  $C^2H^2(OH^2)O^2$ , is a liquid boiling between  $134^{\circ}$  and  $137^{\circ}$ , having a sp. gr. of 1.154 at  $0^{\circ}$ , and an odour like that of acetone. With acid sodium sulphite it becomes hot, but does not yield a crystalline product.

The structural formula of pyroacemic acid is most probably  $CH^2.CO.CO.OH$ , and that of the methylic ether,  $CH^2.CO.CO(OC^2H^3)$  (Oppenheim, *Deut. Chem. Ges. Ber.* v. 1051).

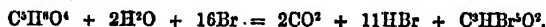
**PYROSULPHOPHOSPHORIC ETHERS.** See SULPHOPHOSPHORIC ETHERS.

**PYROSULPHURIC ACID** and **CHLORIDE.** See SULPHUR, OXYGEN-ACIDS OF.

**PYROVANADATES.** See VANADATES.

**PYROTARTARIC ACID**,  $C^2H^2O^4$ . *Fermentation.*—According to Béchamp (*Compt. rend.* lxx. 299), calcium pyrotartrate fermented in contact with microzymo chalk (1st Suppl. 614) gives off marsh gas and carbon dioxide.

*Action of Bromine* (Lagermark, *Zeitschr. f. Chem.* vi. 299).—Bromine acts very slowly on pyrotartaric acid at ordinary temperatures, but when 10 pts. of pyrotartaric acid, 24 pts. bromine, and 10 c.c. water, are heated together to  $120^{\circ}$ , the bromine disappears in about 6 hours, and on cooling there is obtained (together with  $CO^2$ ), a pale yellow liquid, and mostly a white mass of monobromocitraconic anhydride,  $C^2H^2BrO^3$  (p. 348). On mixing the liquid with 4 or 5 vols. water, crystals separate after some time, consisting of bromoxaform (pentabromomethyl acetate), formed according to the equation:



The bromocitraconic anhydride is supposed to be produced from previously formed dibromopyrotartaric acid; thus:



Bromocitraconic anhydride is also formed, together with a dark greasy mass, when pyrotartaric acid is treated with dry bromine at  $100^{\circ}$ .

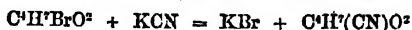
Bromine in presence of water acts but slowly on silver pyrotartrate at ordinary temperatures, but easily at the heat of the water-bath, nothing, however, being produced except pyrotartaric acid, silver bromide, and carbon dioxide. Dry bromine acts on silver pyrotartrate, separating the silver as bromide, and on exhausting with alcohol, and evaporating, there remains a mixture of pyrotartaric acid and anhydride. When 1 mol. pyrotartaric acid is heated with 1 mol. bromine in presence of water, a small quantity of carbon dioxide is evolved, and the only other product formed is bromocitraconic anhydride (soluble in ether), half the pyrotartaric acid (insoluble in ether) remaining unattacked. The same reaction takes place when pyrotartaric acid is treated with an equal volume of bromine without water, excepting that in this case a thick black mass is formed, from which nothing but bromocitraconic anhydride can be separated.

**Tribromopyrotartaric acid**,  $C^2H^2Br^3O^4$ .—The only way of obtaining brominated pyrotartaric acid is to heat the pyrotartaric acid with excess of bromine. 1 mol. of the acid and 5 to 6 mols. bromine are heated in presence of water to  $120^{\circ}$  for three hours, the mixture then left to cool, well shaken, and heated in a flask with a drawn-out neck, till the vapour in the point of the tube appears only light-red; if the process is not conducted in this manner, carbonisation, and still more easily explosion, may take place. On opening the tube, hydrogen bromide and carbon dioxide escape. The resulting solid white mass consists of tribromopyrotartaric acid, which, after washing, pressing and recrystallisation from water, separates from its solution by slow evaporation in six-sided prisms having a strong acid reaction. It does not melt at  $240^{\circ}$ , but sublimes without previous fusion at a higher temperature.

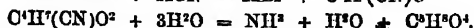
**Silver tribromopyrotartrate**,  $C^2H^2Br^3Ag^2O^4$ , is a white precipitate, insoluble in water,

permanent in the air, anhydrous at 100°. The potassium salt is an amorphous glassy mass, easily soluble in water.

*Isomerides of Pyrotartaric acid.*—Wislicenus (*Ann. Ch. Pharm.* cxlix. 220) has converted bromobutyric acid,  $C^4H^7BrO_2$ , into an acid isomeric with pyrotartaric acid, by treating its ethylic ether first with potassium cyanide, then with potassium hydrate:



and



The products of this reaction are a crystallised acid melting at 111°–112°, and, in larger quantity, a syrupy acid whose neutral ammonia salt is precipitated by lead and mercuric salts, but not by zinc, copper, cadmium, or ferric salts. Both these acids have the composition  $C^4H^7O_4$ . Hence Wislicenus infers that in the bromination of butyric acid, two isomeric acids are formed—namely,  $\alpha$ -bromobutyric acid,  $CH^3.CH^2.CHBr.CO^2H$ , which may be converted into syrupy ethyl-malonic acid,  $CH^3.CH^2.CH(CO^2H)^2$ ; and, in smaller quantity,  $\beta$ -bromobutyric acid,  $CH^3.CHBr.CH^2.CO^2H$ , which, by the process above described, is converted into another isomeride of pyrotartaric acid represented by the formula,  $CH^3.CH(CO^2H).CH^2.CO^2H$ . The first of these isomeric acids has likewise been obtained from  $\alpha$ -bromobutyric acid by Markownikoff and Tupoleff (*Deut. Chem. Ges. Ber.* v. 329), who find that it is resolved by heat into butyric acid and carbon dioxide.

**PYRRHITE.** According to A. Schrauf (*Jahrb. f. Mineralogie*, 1871, 764), the pyrrhite of San Miguel (zirconium niobate, iv. 783) exhibits distinct octohedral faces. Hardness = 5.5. A characteristic blowpipe reaction, serving especially to distinguish pyrrhite from pyrochlore, is that pyrrhite forms with microcosmic salt in the oxidising flame a bead which is perfectly clear and colourless, whether hot or cold, whereas the bead formed by pyrochlore is yellow while hot, and becomes colourless only on cooling.

**PYRROL.** Pyrrol-bases appear to be present, together with bases of the pyridine series, in tobacco-smoke (see **TOBACCO**).

*Pyrrol-red*,  $C^{12}H^{10}O_2$ , is formed by the action of acids on tetraphenol (p. 1032).

## Q

**QUARTZ.** This mineral has been found, together with iron-glance, in the clefts of a trachytic lava from Lipari, in small crystals exhibiting all the marks of volcanic sublimation (*G. vom Rath, Pogg. Ann.* cxlvii. 272).

The formation of quartz in small prisms, together with that of a felspar allied to oligoclase, has been observed by H. Benrath (*Jahresb. f. Chem.* 1871, 1139) during the devitrification of lime-soda glasses.

The colour of *smoky quartz* (smoky topaz) has sometimes been attributed to allotropic modification of the silica. Flückiger (*Jahresb.* 1871, 1199), on the other hand, from the examination of very large crystals of smoky quartz from the Tiefen glacier in Switzerland, concludes that the colour is due to organic matter; and this conclusion has been confirmed by A. Forster (*Pogg. Ann.* cxliii. 173), who has shown, by optical examination and determination of density, that the colour cannot be due to allotropic modification, and that the smoky quartz, when subjected to dry distillation, yields a small quantity of a brownish liquid containing ammonium carbonate, whence it would appear that the colour is due to an organic body containing nitrogen.

On the crystalline forms of quartz from various localities, see *Jahresb. f. Chem.* 1870, 1277; 1871, 1138.

**QUARTZ-PORPHYRY.** The following are analyses of this rock from the neighbourhood of Teplitz in Bohemia (*Wien. Akad. Ber.* [2 Abth.], lxi. 755; lxiii. 325):

A. From a quarry. Coarse-grained ground-mass, enclosing numerous quartz-grains and a small quantity of black mica. Sp. gr. = 2.64. Analysed by J. Stingl.

B. Near the foot of the Königshöhe. Decomposed. The ground-mass contains kaolinised orthoclase and coarse-grained quartz. Sp. gr. = 2.58. a. Soluble. b. Insoluble. Analysed by H. Wieser.

C. From the banks of the Saubach. Completely disintegrated. Sp. gr. = 2.512.  
a. Soluble. b. Insoluble. Analysed by J. Stingl.

D. Another variety from the banks of the Saubach. Sp. gr. = 2.567. Analysed by J. Stingl.

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	MnO	CaO	MgO	K <sup>2</sup> O	Na <sup>2</sup> O	H <sup>2</sup> O	
A.	73.09	11.61	7.62	0.88	—	0.90	3.19	2.19	0.70	= 100.27
B. { a.	0.30	3.00	0.45	—	—	—	0.58	1.66	3.20	= 99.34
b.	67.81	20.47	0.85	—	1.46	0.06	—	—	—	
C. { a.	—	—	5.62	—	—	—	—	—	—	= 100.34
b.	76.52	10.30	6.30	—	—	—	1.60	—	—	
D.	75.47	15.07	3.86	—	0.95	0.63	1.85	0.51	1.43	= 99.77

**QUININE. QUINIDINE. QUINICINE. QUINAMINE.** See CINCHONABASMS (pp. 343-346).

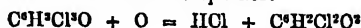
**QUINOA.** The bitter seeds of red quinoa, grown in the gardens of Lima, were found by M. C. Cooke (*Pharm. J. Trans.* [3], iii. 281) to contain:

	per cent.		per cent.
Water . . . . .	16.01	Casein and a small quantity	
Starch . . . . .	38.72	of insoluble albumin . . .	7.47
Sugar and extractive		Insoluble albumin and other	
matters . . . . .	5.12	proteids . . . . .	11.71
Gum . . . . .	3.94	Vegetable fibre . . . . .	7.99
Oil . . . . .	4.81	Inorganic matter . . . . .	4.23

**QUINONE, C<sup>6</sup>H<sup>4</sup>O<sup>2</sup>.** Vapour-density.—Hofmann (*Deut. Chem. Ges. Ber.* iii. 583) has determined the vapour-density of quinone in a barometric vacuum at the temperature of aniline vapour; and has obtained the numbers 51.7 and 53.73 (H=1), agreeing nearly with the number 54 calculated from the formula C<sup>6</sup>H<sup>4</sup>O<sup>2</sup>.

Quinone volatilises completely at the temperature of boiling aniline; its vapour has a faint yellow colour, and condenses, on cooling, in long yellow needles, which exhibit no sign of decomposition.

**Dichloroquinone, C<sup>6</sup>H<sup>2</sup>Cl<sup>2</sup>O<sup>2</sup>,** is formed, with evolution of hydrochloric acid, by the action of nitric or nitrous acid on trichlorophenol:



(Faust, *Zeit. f. Chem.* 1867, 727; Weselsky, *Deut. Chem. Ges. Ber.* iii. 646). It crystallises from alcohol in straw-yellow prisms an inch long; has a peculiar aromatic odour; colours the skin reddish-brown; melts at 120°; sublimates at a much lower temperature; and gives, with ammonia, a solution gradually turning green, reddish, and finally brown, from which acids no longer precipitate dichloroquinone. Ferric chloride added to its aqueous solution throws down slender white needles (Faust).

**Dichlorodioxyquinone. Chloranilic acid, C<sup>6</sup>Cl<sup>2</sup>(OH)<sup>2</sup>O<sup>2</sup>.**—This substance, fused with potash at 150°–170° in a stream of hydrogen, yields potassium chloride and oxalic acid. When potassium chloranilate is heated to 170° with potassium acetate and water, or with water alone, carbon dioxide is formed and a large quantity of carbon separated. Potassium chloranilate detonates when heated alone, likewise yielding carbon dioxide and free carbon:

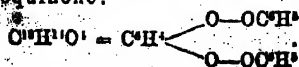


(Morz a. Woith, *Deut. Chem. Ges. Ber.* v. 462).

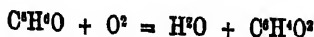
**Hydroquinone, C<sup>6</sup>H<sup>4</sup>O<sup>2</sup> = C<sup>6</sup>H<sup>4</sup>(OH)<sup>2</sup>.**—On the structure of this compound and its isomerides, pyrocatechin and resorcin, see PHENOLOLS (p. 924); also Hesse (*Deut. Chem. Ges. Ber.* v. 1022; *Chem. Soc. J.* [2], xi. 386).

Hydroquinone heated with phthalic and sulphuric acids forms a red phthalein, which dissolves in potash with a red colour, and dyes iron and alumina mordants like barwood (Grabowsky, *Deut. Chem. Ges. Ber.* iv. 658).

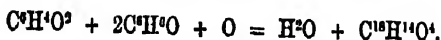
**Phenoguinone.** When 1 pt. of phenol, C<sup>6</sup>H<sup>5</sup>O, dissolved in water, is digested with 2½ pts. chromic acid for half-an-hour, chromic oxide separates, and on distilling the solution, a yellow watery liquid passes over; and on agitating this with ether and evaporating the ethereal solution, a dark-red crystalline mass is obtained which, by pressure and sublimation, yields beautiful red needles, with green metallic lustre, consisting of phenoguinone:



The formation of this substance is due to the oxidation of part of the phenol to quinone, and the combination of this body with phenol deprived of 2 at. hydrogen by further oxidation:



and

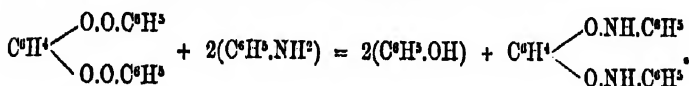


In fact, on adding quinone to a solution of phenol, the same red compound is obtained, but various reduction-products are formed at the same time, including apparently green quinhydrone.

Phenoquinone melts at 71°, dissolves in water, more readily in alcohol and ether; it is not altered by chromic acid in the cold; does not form salts. It splits up, under the influence of heat and of various reagents, into phenol and quinone, or the products of their decomposition (Wichelhaus, *Deut. Chem. Ges. Ber.* v. 248).

All the phenols of the aromatic series (cresol, thymol, resorcin,  $\alpha$ -naphthol,  $\beta$ -naphthol, &c.) react with quinone in a similar way; thymoquinone also reacts thus, but the difficultly reducible anthraquinone does not undergo such changes. Chloroquinone and thiophenol do not develop substitution-products in this manner; trichlorinated quinone is reduced, and the chlorine removed, by the action of pyrogallie acid; tetrachloroquinone, on the other hand, does not lose any chlorine, but forms tetrachloro-hydroquinone; thiophenol reduces the quinone to quinhydrone, and finally to hydroquinone.

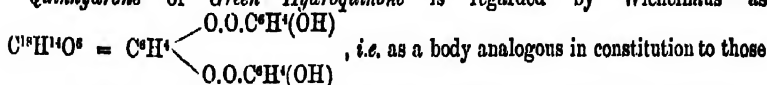
Phenoquinone, treated with *aniline*, forms a crystalline product similar in constitution to itself, being derived from it by substitution of NH for O:



This body is identical with Hofmann's quinone-anilide, obtained by the action of quinone on aniline. Hofmann regarded it as  $C^{12}H^{14}O^2N^2$ , whereas Wichelhaus assigns to it the above formula,  $C^{12}H^{14}O^2N^2$ .

*Pyrogallol* dissolves quinone, producing red crystalline pyrogallol-quinone,  $C^6H^4[O.O.C^6H^4(OH)^2]^2$ , already described (p. 1030).

*Quinhydrone* or *Green Hydroquinone* is regarded by Wichelhaus as



above considered. This formula agrees well with Wöhler's analysis of quinhydrone; nevertheless, this body is generally regarded as  $C^{12}H^{10}O^4 = C^6H^4O^2.C^6H^4O^2$  (Wichelhaus, *Deut. Chem. Ges. Ber.* v. 840).

On *Naphthaquinone*, see p. 825.

On the isomeric bodies, *Anthraquinone*, *Phenanthrene-quinone*, and on the constitution of Quinones in general, see pp. 90-95.

**QUINTANES,  $C^6H^{12}$ .** See AMYL HYDRIDES (p. 63). It is there suggested that tetramethyl-methane,  $C(CH^3)^4$ , might be obtained by the action of zinc-methyl on dichloropropane or methyl-chloracetol,  $CH^3-CCl^2-CH^3$ ; and indeed Lwow (*Zeitschr. f. Chem.* [2], vii. 257) has actually obtained by this process a gas having the composition  $C^6H^{12}$ ; but it does not crystallise at  $-30^\circ$ , whereas that which he formerly obtained by the action of zinc-methyl on tertiary butyl iodide (*ibid.* vi. 521) solidified at  $-20^\circ$ . The later product was perhaps impure.

## R

**RABDIONITE.** A soft black graphic mineral, occurring in the form of small bars at Nischne-Tagilsk in the Ural. When rubbed with the finger, it acquires a fatty lustre. It melts easily before the blow-pipe to a steel-grey magnetic bead, by which property and by its large amount of iron it is distinguished from asbolan. Sp. gr. = 2.80. Analysis gave:

FeO*	MnO*	Al <sub>2</sub> O <sub>3</sub> *	CaO	MnO	CaO	H <sub>2</sub> O
45.0	18.00*	1.40	14.0	7.61	5.10	13.50 = 99.61

\* Another experiment gave 14.00.

(F. v. Kobell, *J. pr. Chem.* [2], i. 428).

**RACEMIC ACID.** On the reciprocal transformation of racemic and inactive tartaric acid, see TARTARIC ACID.

**RAIN.** On the composition of Rain-water, see ATMOSPHERE (p. 112). On the quantities of nitrous and nitric acid in rain-water, see NITRIC ACID (p. 857); also *Chem. Soc. J.* [2], x. 87, 281, 324.

**RALSTONITE.** A hydrated aluminium fluoride containing traces of sodium and calcium, from the cryolite formation of Arksut Fjord in Greenland. It crystallises in regular octohedrons (sometimes with very subordinate dodecahedral faces); colourless, and with a vitreous lustre. Hardness above 45. Sp. gr. = 2.4. It appears to be chemically related to *fluellite*, which crystallises in rhombic forms (G. J. Brush, *Sill. Am. J.* [3], ii. 30).

**RAMMELSBERGITE** (F. Sandberger, *Jahrb. f. Mineralogie*, 1871, 935).—This mineral, the rhombic form of nickel diarsenide, NiAs<sub>2</sub>, hitherto found only at Schneeberg in Saxony, has lately been found at Wittichen in Baden. A specimen analysed by A. Hilger gave results agreeing nearly with the former analysis by E. Hofmann (iv. 37).

	As	Ni	Fe	Bi	Cu	Co	S
Hilger	68.80	26.65	2.06	2.66	trace	trace	trace = 99.67
Hofmann	71.30	28.14	—	2.19	0.50	—	0.14 = 102.27

Deducting the bismuth, and reckoning the iron as nickel, both analyses lead to the formula NiAs<sub>2</sub>, which requires 72.15 p.c. As, and 27.85 Ni. The mineral becomes covered by weathering with a very light green crust, appearing under the microscope as a mixture of glistening white octohedrons of arsenious oxide and green lustreless nickel arsonate (nickel-bloom).

In the specimen analysed by Sandberger the rammelsbergite is coated with a crust of steel-grey smaltine, CoAs<sub>2</sub>, which is intimately mixed with quartz, very hard, and shoots out on the surface into larger crystals,  $\infty$  O $\infty$ . O. Besides cobalt and arsenic, it contains a large quantity of iron, with very little nickel, copper, and sulphur. It is evidently identical with the mineral from the Sauschwart mine at Schneeberg, analysed by E. Hofmann, and containing 0.66 p.c. S, 1.39 Cu, 0.01 Bi, 70.37 As, 11.71 Fe, 1.79 Ni, and 13.95 Cu. The surface of separation of the two minerals does not exhibit a regular curvature, as if one of them had been deposited over the other, but is irregular and jagged, as if the arsenides of the several metals had been first precipitated together, and separated by subsequent molecular action, in such a manner as to concentrate the nickel in the interior. Precisely similar appearances are presented in the occurrence of copper-nickel with smaltine and cloanthite, the copper-nickel forming the irregularly bounded nucleus of a spheroid, and containing only traces of cobalt, which, on the other hand, is concentrated with the iron, and without any nickel, in the outer crust. A specimen from Wittichen was found to contain:

	Ni	Co	Fe	S	As
In the nucleus (copper-nickel)	43.86	trace	0.67	1.18	53.40
In the crust (smaltine)	8.52	10.11	5.05	4.71	89.70

**RAPAKIVI or RABAKIWI.** A variety of granite occurring at Pyterlak and other localities in Finland (v. 77). Analyses  $\alpha$  and  $\delta$  are by Struve;  $\epsilon$  by Benrath, of a weathered friable variety from Pyterlak.

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O
75.06	0.36	11.70	1.04	1.57	trace	1.01	0.19	6.25	2.56	0.63 = 100.37
77.91	0.48	10.13	1.41	2.15	trace	1.13	0.21	4.50	1.85	0.44 = 100.06
74.24	12.13	2.38	—	—	0.90	0.19	6.68	2.56	0.04	100.00

For Benrath's experiments on the manufacture of glass by fusing mixtures of this rock with limestone, see *Dingl. pol. J.* cxv. 264; *Jahresb. f. Chem.* 1870, 1160.

**REDONDITE.** A phosphate from the island of Redondas, West Indies. It is amorphous, resembles allophane, but is sometimes translucent, from porosity, to opaque; greenish to yellowish white, rarely with milk-white spots. Fracture conchoidal to earthy; the earthy varieties adhere strongly to the tongue. Hardness 3·5 to 4. Sp. gr. 1·90–2·07. The mineral contains, in addition to traces of  $\text{SO}_3$ , Na, Cl and Mg:

$\text{P}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$	$\text{SiO}_2$	$\text{CaO}$
43·20	14·40	16·60	24·00	1·60	0·67 = 100·37

(C. U. Shepard, *Sill. Am. J.* [2], xlvii. 428). Another specimen gave sp. gr. = 2·019, perhaps too high on account of admixed silica (8·8 p.c.); it contained 24·73 p.c. water and 40·19  $\text{P}_2\text{O}_5$ , or, after making the necessary allowance for impurities, 44·07 (*ibid.* 1. 06).

**REFRACTION.** See LIGHT (p. 741).

**REGIANIN.** A substance obtained from the green shell of the walnut (*Juglans regia*). It may be extracted by benzene, and crystallises in yellowish elongated octohedrons or feathery groups of prisms. It is easily decomposable, and forms, with the fixed alkalis and ammonia, solutions of a fine purple-red colour, from which acids throw down brown flocks. By redissolving these in weak soda-ley, precipitating with hydrochloric acid, and washing with boiling water, regianic acid,  $\text{C}^8\text{H}^6\text{O}_7$ , is obtained as a dense amorphous pitch-black powder insoluble in water, soluble with purple-red colour in alkalis. It forms a brown lead salt,  $\text{PbO}, \text{C}^8\text{H}^6\text{O}_7$ , a pitch-black silver salt, and a flesh-coloured lime salt, which is precipitated by boiling its solution with a small quantity of ammonia (Philpson, *Chem. News*, xxiv. 119).

**REISSITE.** A zeolitic mineral occurring, together with quartz and desmin, in a trachytic conglomerate on Thera (Santorin), in short prismatic crystals belonging to the rhombic system. It is transparent and colourless, or whitish with a vitreous lustre, melts easily, dissolves after heating more easily than before, with separation of a jelly. The solution contains lime and alkalis (K. v. Fritzsche, *Jahrb. f. Mineralogie*, 1870, 80). According to Hesseberg's measurements (*ibid.* 480), the crystals exhibit the combination  $\infty \text{P} : \infty \text{P} \infty : 2\text{P}^2$ . Angle  $\infty \text{P} : \infty \text{P} = 134^\circ 8'$ . Cleavage parallel to the brachydiagonal.

**RESINS, FOSSIL.** H. Spirgatis (*N. Rep. Pharm.* xx. 321) has examined a fossil resin from the coast of the Baltic, near Brusterort. It is commonly known as 'unripe amber,' but differs essentially from amber by the absence of succinic acid; on the other hand, it exhibits several points of resemblance to Krantzite (iii. 448). It is inodorous, light yellow or greenish, nearly transparent, but covered with a thin opaque crust. When heated it burns with a bright smoky flame, leaving 0·33 p.c. ash. It becomes darker at  $100^\circ$ , and melts above  $300^\circ$ . Sp. gr. = 0·934. Analysis gave 86·02 p.c. carbon, and 10·93 hydrogen, agreeing with the formula,  $\text{C}^{10}\text{H}^{12}\text{O}$ , which requires 86·02 C, 11·11 H, and 2·87 O.

**Rosthornite** (H. Hüfer, *Jahrb. f. Mineralogie*, 1871, 561). This resin occurs in the coal-beds of the Sonnberg, near Guttaring in Carinthia. It has a fatty lustre, a brown colour with garnet glimmer, wine-yellow by transmitted light, especially in splinters, and a light-brown to orange-yellow streak. It is brittle and may be scratched with the nail. Sp. gr. = 1·076. When heated in the air, it gives off white vapours having an aromatic odour, and burns with a deep yellow smoky flame, without leaving any residue. At  $96^\circ$  it begins to melt to a viscid, brown-red mass, which throws up bubbles at  $160^\circ$ , and emits white vapours from  $215^\circ$  to  $225^\circ$ , at which latter temperature the mass becomes mobile, assumes a dark purple-red colour, and emits a fetid gaseous mixture, but does not give off succinic acid. When fused with alkaline carbonates, it does not exhibit any trace of sulphur, although that element is present in the coal in the immediate neighbourhood of the resin. Rosthornite is not altered by dilute nitric acid, by potash-ley, or by alcohol, either in the cold or on boiling; in warm ether, however, it dissolves partially, forming a turbid wine-yellow solution, and leaving a white tumefied residue. In cold turpentine-oil it remains unaltered, but hot turpentine-oil dissolves the pure resin almost entirely, leaving only a small quantity of dark-coloured matter (enclosed particles of coal). It swells slightly in cold and dissolves partially in hot petroleum. In benzene it dissolves at ordinary temperatures, forming a clear dark wine-yellow liquid.

Rosthornite in its physical characters bears considerable resemblance to jaulingite and pyroretin, but in chemical composition it approaches more nearly to euosmite, and still more to the fossil resin of Girona, near Bucaramanga in New Granada, as will be seen from the following comparison:—

	Rosthornite	Janlingite	Eucemite	Girona resin
Carbon . . .	84.42	74.43	81.89	82.7
Hydrogen . .	11.01	9.04	11.73	10.8
Oxygen . . .	4.57	16.53	6.38	6.5
	100.00	100.00	100.00	100.0

Eucemite is distinguished from rosthornite by its strong odour of camphor and rosemary, by its easy and complete solubility in alcohol and ether, and by the deep yellow colour which it imparts to potash-ley, &c. Pyroretin also differs from rosthornite in its behaviour to solvents, and moreover contains 10 p.c. oxygen. Girona or Bucaramanga resin, which occurs in auriferous porphyritic alluvians, resembles rosthornite in its behaviour to alcohol and ether, but is transparent, pale yellow, and very much like amber in its physical characters.

Rosthornite, therefore, cannot be included either physically or chemically in the succinite group, or in that of retinite (80.4 C; 10.7 H; 8.7 O), neither on chemical grounds can it be referred to the ixolite group, to which janlingite belongs. It appears rather to form a type of solid resins rich in carbon and poor in oxygen.

**Fossil Resin from the Val d'Arno Superiore** (I. Guaroschi, *Cimento*, v.-vi. 175). The lignites of the Figliano basin on the left bank of the Arno contain several fossil resins, one of which is called by the country people 'combustibile earth' (*terra che bruccia*). This resin is a light, very friable, amorphous, yellowish-white mass, which burns like touchwood, and with a somewhat smoky flame. It contains 41.3 p.c. organic and 58.7 mineral substance, the latter consisting of silica, ferric oxide, alumina, manganese oxide (trace), lime, magnesia, potash and soda, soluble in hydrochloric acid; and silica, iron silicate, and aluminium silicate, insoluble in that acid.

The organic matter is almost wholly soluble in alcohol, and may be resolved, by fractional solution in that liquid, into two resins,  $\alpha$  and  $\beta$ , having the following composition:—

	O	H	O
Resin $\alpha$ . . .	72.72	9.41	17.87 = 100
Resin $\beta$ . . .	76.94	9.12	13.94 = 100

The composition of  $\alpha$  agrees nearly with the formula  $C^{40}H^{14}O^8$ , that of  $\beta$  with  $C^{40}H^{13}O^8$ . The resin  $\alpha$  may be supposed to have been formed by oxidation of a polymeride of turpentine-oil,  $4C^{10}H^{14} + O^8 = C^{40}H^{14}O^8$ , and  $\beta$  by abstraction of the elements of water from  $\alpha$ :  $C^{40}H^{14}O^8 - 3H^2O = C^{40}H^{13}O^8$ . Both exhibit considerable analogy, both geologically and chemically, to the group of resins called *pyropissite*, from the lignite of Weissenfels (iv. 769).

Resin  $\alpha$  is blackish when melted, yellowish in powder, lighter than water, softens at 75°, and melts completely at 90°. It dissolves with brown colour in alcohol, very easily in benzene and in turpentine-oil, very slightly in ether. Strong sulphuric acid dissolves it in the cold, more easily when heated. Nitric acid acts but slowly, or not at all, upon the resin itself; but when added to the sulphuric acid solution it appears to form a nitro-substitution product. By melting the resin with potash, no organic acid is formed, but merely an alkaline carbonate. By distillation the resin yields a brown empyreumatic liquid which does not appear to contain succinic acid.

Resin  $\beta$  is blackish and amorphous, very slightly soluble in alcohol, much more freely in benzene and turpentine-oil. It is lighter than water, melts at a temperature above 120°, and is soluble in potash.

**RESORCIN**,  $C^6H^4O^2 = C^6H^4(HO)^2$ . This modification of dioxybenzene, formerly regarded as a para-compound, is now placed in the meta or isophthalic series (see *PERAZOL*, p. 924).

Resorcin is formed by the dry distillation of brazilin (p. 208), and may be easily prepared by mixing the wash- and mother-waters obtained in the manufacture of brazilin from Brazil-wood extract, with chalk, evaporating to dryness, and subjecting the residue to dry distillation. This, according to E. Kopp, is the easiest and cheapest of all methods of preparing resorcin.

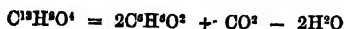
Resorcin melts at 98°–99° and distils at 266°–267°. A very characteristic test for it is to treat a small quantity with *fuming sulphuric acid*, which dissolves it with an orange-yellow colour, gradually darkening and changing in 20–30 minutes to greenish-blue, and ultimately to a pure blue: on warming the liquid to 90°–100° this blue changes to a fine purple-red (E. Kopp, *Deut. Chem. Ges. Ber.* vi. 446).



A mixture of resorcin with *furfural*, touched with a drop of hydrochloric acid, forms an indigo-blue substance which dissolves with green colour in water, and is precipitated by hydrochloric acid in blue flocks (A. Baeyer, *Deut. Chem. Ges. Ber.* v. 25).

*Benzoin aldehyde* reacts with resorcin in the same way as with pyrogallol (p. 1031).

Resorcin heated to  $195^{\circ}$  with *phthalic anhydride* yields resophthalein or fluorescein,  $C^{12}H^{10}O^3 = 2C^6H^4O^2 + C^6H^4O^2 - 2H^2O$  (p. 524). Heated with *succinic anhydride*, it yields a yellow, resinous substance, similar in character to fluorescein, and doubtless consisting of the succinein of resorcin,  $C^{12}H^{10}O^3 = 2C^6H^4O^2 + C^6H^4O^2 - 2H^2O$ . Heated with *oxalic* and *sulphuric acids*, it yields a yellow substance, which differs from the phthalein and succinein just mentioned in forming a non-fluorescent solution, and appears to be identical with euxanthone (1st *Suppl.* 610), which may accordingly be regarded as the carbonein of resorcin:



(Baeyer, *Deut. Chem. Ges. Ber.* iv. 682).

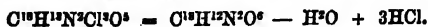
**Azo-derivatives of Resorcin** (Weselsky, *Deut. Chem. Ges. Ber.* iv. 613). *Diazo-resorcin*,  $C^{12}H^{12}N^2O^4$ , is formed by the action of nitrous acid on an ethereal solution of resorcin:



It forms brown granular crystals, with a green metallic lustre; is sparingly soluble in water, dissolves more freely in alcohol and acetic acid, with a dark cherry-red colour, and its alkaline solutions have a splendid blue-violet colour. By the action of strong sulphuric or hydrochloric acid it is converted into diazo-resorufin,  $C^{12}H^{12}N^2O^4$ , which separates from the hydrochloric acid solution in small, dark red, granular crystals. It is nearly insoluble in water, alcohol and ether; concentrated sulphuric acid dissolves it with a crimson colour, and the same colour is exhibited by its alkaline solutions, which have also a beautiful vermilion-red fluorescence.

When diazo-resorcin is heated with tin and strong hydrochloric acid, the solution assumes an emerald-green colour, and on cooling, hydro-diazo-resorufin hydrochloride,  $C^{12}H^{12}N^2O^4.H^2 + 3HCl$ , crystallises out in the form of green leaflets with a silvery lustre, or of light green needles. The crystals, when exposed to the air, assume the colour and the coppery lustre of indigo. On heating this compound in a current of air, the hydrochloric acid escapes, and oxidation takes place, diazo-resorufin being reproduced. When a solution of the hydrochloride is heated with diazo-resorufin, a dark-blue solution is obtained, from which dark bottle-green, shining needles crystallise out, which are a combination of the two substances, analogous to quinchidrone.

By heating diazo-resorcin with acetyl chloride in closed tubes, dehydro-diazo-resorcin hydrochloride is formed:



It crystallises in yellow scales, resembling mosaic gold, insoluble in water but soluble in alcohol with a straw colour, and in alkalis with a magnificent violet. By cold nitric acid it is converted into a brick-red flocculent body, which, when treated with warm nitric acid, gives purple plates, the alcoholic or ethereal solution of which shows a remarkable vermilion-red fluorescence. Both compounds are true colouring matters, and the former has the property that the fluorescence of its ammoniacal solution appears also on silk dyed with it. The above reaction of acetyl chloride also gives rise to acetyl-diazo-resorcin, in the form of an amber-yellow resin.

By heating diazo-resorcin with strong nitric acid tetrazo-resorcin nitrate,  $C^{12}H^{12}N^4O^6(NO^3)^2$ , is obtained:

1.  $C^{12}H^{12}N^2O^3 + N^2O^3 = 3H^2O + C^{12}H^{12}N^4O^6$
2.  $C^{12}H^{12}N^4O^6 + 3N^2O^3 = 3NO^2 + C^{12}H^{12}N^4O^6(NO^3)^2$ .

This nitrate crystallises in well-defined garnet-red needles, which have a brilliant metallic lustre, dissolve in water and alcohol, and very readily in ether with a pure indigo-blue colour. By further action of nitric acid, tetrazo-resorufin nitrate,  $C^{12}H^{12}N^4O^6(NO^3)^2$ , is formed. The crystals contain water, have the appearance of potassium permanganate, and dissolve with the same colour in water, alcohol, and ether. On drying, the water of crystallisation escapes, and a dull, brick-red powder is left behind. On boiling it with water, decomposition takes place, which is accelerated in presence of alkalis; from the brown solution dark flakes separate out. By the action of nascent hydrogen, it is transformed into dihydro-tetrazo-resorufin nitrate,  $C^{12}H^{14}N^4O^6H^2(NO^3)^2$ , which crystallises from its cherry-red alcoholic solution in small needles.

2nd *Sup.*

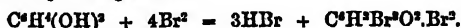
**Hydroamido-tetrazo-resorufin**,  $C^{17}H^{22}N^4O^3 \cdot 6NH^2 \cdot 9HCl$  is the final product obtained by heating any of the above tetrazo-compounds with tin and hydrochloric acid. It crystallises in long, colourless needles, which, on exposure to the air, assume a rose colour; in alkalis it dissolves with a blue colour. By passing air through the ammoniacal solution, it becomes brown, whilst green crystals, with a cantharidic reflection, separate out. This body is *hydro-imido-tetrazo-resorufin*,  $C^{16}H^{22}N^4O^3(NH)^2$ ; it is insoluble in water, and dissolves in concentrated hydrochloric and diluted nitric acid, with a wine-red colour.

**Bromoresorcins.** *Pentabromoresorcin*,  $C^6HBr^5O^2$ , is prepared by adding an aqueous solution of resorcin, with constant agitation, to a cooled mixture of bromine and water (in the proportion of about 5 : 1). By two or three crystallisations from carbon sulphide it is obtained pure in large colourless or sulphur-yellow prisms. It melts at  $113.5^\circ$ , is nearly insoluble in water, dissolves easily in ether and in alcohol, moderately in benzene. From solution in hot petroleum oil it separates for the most part on cooling. *Hydriodic acid* converts it into a compound which crystallises in colourless needles; probably tribromoresorcin (Stenhouse, *Ann. Ch. Pharm.* clixiii. 182).

The composition of pentabromoresorcin appears to be at variance with Kekulé's theory of the constitution of the dioxybenzenes,  $C^6H^2O^2$ , according to which one of the five hydrogen atoms which are replaced by bromine to form the compound,  $C^6HBr^4O^2$ , should exist in the form of hydroxyl, and should therefore not be thus replaceable. This difficulty suggested to Liebermann n. Dittler (*Deut. Chem. Ges. Ber.* v. 1090) the idea that the compound in question might be really an addition-product,  $C^6H^2Br^4O^2 \cdot Br^2$ , containing 2 at. hydrogen more than are assigned to it by Stenhouse. To decide this point they determined the quantity of bromine required for its formation, and the quantity of hydrobromic acid evolved thereby. The result showed, however, that the reaction takes place exactly as stated by Stenhouse, that is to say, according to the equation:



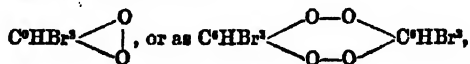
and not as represented by the equation:



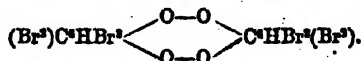
Liebermann n. Dittler also find that pentabromoresorcin heated to  $150^\circ$ – $160^\circ$  gives off 2 at. bromine according to the equation:



leaving a substance which, after washing with ether to remove a little resinous matter, forms a crystalline powder having the composition  $C^6HBr^3O^2$ . This body may be regarded as tribromoresorcin-quinone:



and pentabromoresorcin may then be regarded as the additive compound:



It is, however, quite possible that tribromoresorcin-quinone may be derived from a pentabromoresorcin having the constitution  $C^6HBr^3 \begin{array}{c} \diagup OBr \\ \diagdown OBr \end{array}$ .

**Chlororesorcins.** *Pentachlororesorcin*,  $C^6HCl^5O^2$ , is best prepared by adding alternately in small portions 5 pts. potassium chlorate and a solution of 2 pts. resorcin in 8 pts. hydrochloric acid to 40 pts. of hydrochloric acid, keeping the potassium chlorate always in excess, and cooling the mixture to prevent too great a rise of temperature. The crude product which separates on leaving the liquid at rest, appears to consist mainly of a hydrate of chlororesorcin; for on heating it with a small quantity of carbon sulphide, and filtering the solution quickly, small white crystalline scales separate out, which are but sparingly soluble in carbon sulphide; and on distilling the carbon sulphide solution, water passes over, and the concentrated liquid now deposits anhydrous pentachlororesorcin in shining colourless prisms or thin prisms. By one or two re-crystallisations it may be obtained pure. It melts at  $92.5^\circ$  is moderately soluble in hot water, and separates therefrom on cooling evidently a hydrate, in the form of a white, opaque mass, in which no crystals can be detected.

recognised. It dissolves easily in carbon sulphide, benzene and petroleum-oil, still more easily in alcohol and ether (Stenhouse, *Ann. Ch. Pharm.* clxiii. 182; *Proc. Roy. Soc.* xx. 78).

Pentachlororesorcin is converted by hydriodic acid into a crystalline compound, which appears to be trichlororesorcin (Stenhouse, *Chem. News*, xxiii. 230).

**Iodoresorcin**,  $C^6H^3IO^2$ , is prepared by agitating an ethereal solution containing 1 mol. resorcin to 1 mol. iodine, with dry precipitated mercuric oxide, or better with litharge, then distilling off the ether, and exhausting the residue with hot benzene. Iodoresorcin then separates on cooling in the crystalline state, and may be purified by two or three alternate crystallisations from benzene and hot water. It is a colourless, crystalline body, resembling iodorein (p. 879) in its general characters, but much more soluble in water (Stenhouse, *Chem. News*, xxvi. 179).

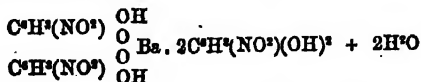
**Nitroresorcins.** *Mononitroresorcin*,  $C^6H^3(NO^2)O^2$ , is contained in considerable quantity in the ethereal mother-liquors obtained in the preparation of diazo-resorcin. To separate it, the resinous residue is boiled with water, and the filtered solution mixed with lead acetate, whereby a dirty-brown precipitate is formed. From the filtrate from this precipitate, the excess of lead is removed by sulphuric acid, and the yellow liquid is shaken up with ether, which, on evaporating, leaves the crude nitroresorcin as a crystalline mass. This is pressed and dissolved in water, and the solution is saturated with baryta-water and left to cool, whereupon the neutral barium salt of nitroresorcin crystallises out in long needles. The solution of this salt, decomposed by sulphuric acid, is exhausted by ether, and the residue left when the ether evaporates is purified by recrystallisation from hot water.

Mononitroresorcin crystallises from hot water or from alcohol in long capillary, folded, thread-like, lemon-yellow needles, which do not taste bitter, are not explosive, and cannot be sublimed without decomposition. Its melting point is  $115^\circ$ . In hot water it melts to an oil before dissolving.

The neutral *barium compound*,  $C^6H^3(NO^2)O^2Ba + 5H^2O$ , crystallises from hot water in tufts of needles, often half an inch long, and having the colour of potassium dichromate. By slow separation from more dilute solutions, thicker prisms are obtained, having the aspect of potassium ferricyanide, and a bluish metallic lustre. According to Ditscheiner's measurements, they very probably belong to the triclinic system. Combination:  $\infty P' : \infty P : \infty \bar{P} \infty : \bar{P} \infty : P \infty$ . Angle  $\infty P' : \infty \bar{P} \infty = 117^\circ 30'$ ;  $\infty P' : \infty P$  right behind =  $129^\circ 50'$ ;  $\infty P' : \infty P = 50^\circ$ ;  $\infty P \infty : \infty P' = 111^\circ 50'$ . The faces  $\bar{P} \infty$  and  $P \infty$  are deeply striated.

The *monobasic barium compound*,  $[C^6H^3(NO^2)(OH)O]^2Ba + H^2O$ , is obtained by passing carbon dioxide into the hot solution of the preceding salt. It crystallises in drusy aggregates of dark yellow, slender needles, which are more soluble in water than the preceding salt.

An *acid barium compound* represented by the formula:



separates from a solution of the neutral salt mixed with acetic acid, in golden-yellow, moderately long, shining, brittle needles, arranged in tufts or stellate groups. It may also be prepared by dividing the hot solution of a weighed quantity of mononitroresorcin into two equal parts, saturating one with barium carbonate and then adding the other. The *potassium salt*, obtained by decomposing the neutral barium salt with potassium sulphate, forms orange-red flat needles, easily soluble in water. The *magnesium salt*, prepared in like manner from the neutral barium salt, crystallises in orange-red, long, capillary, felted needles, somewhat more soluble than the corresponding barium salt (Weselsky, *Ann. Ch. Pharm.* clxiv. 1).

*Dibromonitroresorcin*,  $CHBr^2(NO^2)(OH)^2$ , is obtained by dropping bromine into an ethereal solution of nitroresorcin till the colour no longer disappears, evaporating the ether, and crystallising the residue from alcohol, in yellow laminae resembling iodide of lead. It is also formed by the action of nitric acid containing nitrous acid on an ethereal solution of tribromoresorcin. It melts at  $147^\circ$ . The *barium compound*,  $[CHBr^2(NO^2)(OH)O]^2Ba + 4H^2O$ , forms small orange-red needles, which have a blue reflex, and are very slightly soluble in water (Weselsky).

*Trinitroresorcin*. *Oxypticic* or *Styptic acid*,  $C^6H^3(NO^2)O^2$ .—This compound may be prepared in the same way as trinitroresorcin (p. 879). It crystallises in light yellow laminae melting at  $175.5^\circ$ , dissolves in 156 pts. water at  $14^\circ$ , and is precipitated from this solution by stronger acids, even when added in very small quantity. Its

*barium salt*,  $C^6H(NO^2)_2O^2Ba + 3H^2O$ , forms small, light yellow, rhombic laminae, more soluble in water than the corresponding orcin compound; gives off its water when heated a little above  $100^\circ$ , and explodes with great violence at a higher temperature. The *lead salt* crystallises from hot aqueous solution, in dark, yellow needles; it is slightly soluble in water, easily soluble in acetic acid, and is precipitated from this solution by alcohol. The *silver salt*,  $C^6H(NO^2)_2O^2Ag^2$ , crystallises from hot water in long, slender, yellowish-brown needles (Stenhouse, *Proc. Roy. Soc.* xix. 410).

**RESORCIN-CARBONIZIN**,  $C^6H^2O^4 = 2C^6H^2O^3 + CO - 2H^2O$  (see p. 1041).

**RESORCIN-INDOPHANE**,  $C^6H^2N^2O^4$ . This name is given by J. Schroder (*Ann. Ch. Pharm.* cxliii. 297) to an acid compound, the potassium-salt of which is obtained by the action of potassium cyanide on the potassium salt of trinitroresorcin (potassium styphnate). To prepare this salt, a solution of 20 grams potassium cyanide in 100 c.c. water at  $40^\circ$ - $50^\circ$  is gradually added to a solution of 100 grams of potassium styphnate in a litre of water, heated to  $70^\circ$ - $80^\circ$ ; the heat is continued for 10-15 minutes longer; the liquid quickly filtered through linen; and the separated salt is washed with cold water till the wash-water begins to show a green colour, and then pressed. The filtrate contains a large quantity of potassium nitrite. On adding dilute sulphuric acid to the warm concentrated dark green solution, crude resorcin-indophane separates on cooling in slender needles. For further purification, the pressed crystalline mass is redissolved in boiling water, and the filtered solution is mixed with strong hydrochloric acid, whereby the resorcin-indophane, which cannot be recrystallised from water, is reprecipitated.

Resorcin-indophane thus prepared forms small, anhydrous needles, which exhibit very distinct forms under the microscope, and have a lustre of bronze, changed to that of copper by friction. It dissolves easily, even in cold water, with pure blue-violet colour, is insoluble in alcohol and ether, and is dissolved in not inconsiderable quantity by hot concentrated acetic acid. It likewise dissolves, without decomposition, in cold concentrated sulphuric acid, and is precipitated from the solution by water. When heated in the air, it burns away with slight detonation. Nitric acid converts it into a yellow syrup in which crystals of oxalic acid form on standing. The blue solution of resorcin-indophane is decolorised by *chlorine-water*, and the resulting wine-yellow liquid yields to ether a product which, as the ether evaporates, remains as a resin having the pungent odour of chloropierin.

Resorcin-indophane appears to be completely decomposed by melting *potash*. On heating it with *sodium-anaglam*, the insoluble sodium salt is immediately produced, on which the evolved hydrogen exerts no action. In like manner, on treating it with *tin* and *hydrochloric acid*, the only product is a tin compound, very difficult to purify, and apparently consisting for the most part of the unaltered substance. Resorcin-indophane is not attacked by *acetyl chloride*. When heated with *soda-lime* it gives off only three-fourths of its nitrogen as ammonia, showing that one atom of nitrogen must be contained in it as  $NO^2$ .

*Potassium Resorcin-indophane*,  $C^6H^2K^2N^2O^6 + H^2O$ , crystallises in microscopic needles. After pressing and drying it forms a black-brown mass, acquiring metallic lustre by friction. It dissolves with difficulty in cold water, but completely in boiling water, the solution having a pure green colour like that of alkaline manganates. It cannot be recrystallised from water, for the hot concentrated solution solidifies to a jelly on cooling. On adding *potash* to the solution, the salt separates in its original form. It is quite insoluble in alcohol. On mixing a solution of pure resorcin-indophane with a solution of pure potassium carbonate, a dark flocculent amorphous precipitate is formed, which, after washing with water containing a trace of alkali, dries up to a hard dark-coloured mass, having a green metallic lustre. The water of crystallisation is not given off till the salt is raised to a temperature at which it decomposes with explosion. The *sodium salt*,  $C^6H^2Na^2N^2O^6 + H^2O$ , is analogous in properties to the potassium salt. The *barium salt*,  $C^6H^2Ba^2N^2O^6 + H^2O$ , separates as a dark-coloured precipitate on mixing the solution of the sodium salt with barium chloride.

**RESORCIN-PHTHALIN**,  $C^{12}H^{12}O^3 = 2C^6H^2O^3 + C^6H^2O^3 - 2H^2O$ . Syn. with *FLUORESCIN* (p. 524).

**RESORCIN-SUCOXININ**,  $C^6H^{12}O^3 = 2C^6H^2O^3 + C^6H^2O^3 - 2H^2O$  (p. 1041).

**RESPIRATION.** As far as the chemistry of respiration is concerned, the most important points which remain to be settled are those relating to the so-called 'internal respiration,' and much attention has lately been given to this point. We are, however, still much in the dark as to the substances mainly oxidised in various tissues, and as to the stages of oxidation attained in each; and, in fact, it is yet far from settled.

nately settled how much of the oxidation of the body goes on in the blood itself, and how much in the tissues outside the blood-vessels.

Ester and St. Pierre found that blood obtained from arteries distant from the heart contained much less loose oxygen than blood drawn from arteries nearer to it, and they concluded that the difference was due to great oxidation going on in the arterial blood itself. Both Hirschmann and Pflüger (*Arch. f. d. Gesam. Phys.* 1868) maintain, however, that the difference in loose oxygen which the above observers found does not exist: the latter observer could find no constant difference in the quantity of loose oxygen in the blood of the femoral and carotid arteries of the dog; and Hoppe-Seyler, who finds some difference, makes it much less than Ester and St. Pierre supposed, and believes it due to the action of the arterial walls, and not to reducing matters in the blood itself. On the other hand, Pflüger (*Centralb. f. d. Med. Wiss.* 1867, No. 46) has shown that blood, after removal from the body, very rapidly fixes some of its loose oxygen, and this at first sight would seem to point to a normal rapid oxidation going on in the circulating blood. Using improved methods which enabled him to extract the gases from fresh-drawn blood very rapidly, he found that all the previous estimations of them were erroneous, the oxygen being given too low, and the carbonic anhydride too high; the average quantity of oxygen which he finds in the arterial blood of the dog is 16.0 vols. in 100 vols. of blood, the gas being calculated at 0° C. and 1 M. mercury pressure (= 22-23 vols. at 760 mm). A. Schmidt gets almost exactly the same average quantity. The extremely small difference, if any, as regards its gases, which, as mentioned above, Pflüger has found to exist between blood taken from arteries near the heart, and that from those more distant from it, appears to show that this oxidation, which goes on so rapidly in blood removed from the body, does not go on at anything like the same rate in the circulating blood; the process is probably almost entirely *post mortem*, and due to that partial decomposition of the hæmoglobin which is known to occur in blood exposed to a vacuum, with formation of products which rapidly combine with oxygen. Stale blood (in which the hæmoglobin is partially decomposed), after saturation with oxygen, very rapidly becomes again venous, while fresh blood, left to itself, does so comparatively slowly; this goes to show that the hæmoglobin products are powerful reducing agents, and Pflüger and Zuntz have also proved that the addition of acids (as phosphoric and tartaric), which Preyer found to diminish the quantity of loose oxygen in blood, does so only when they are added in such quantity as to decompose the hæmoglobin, and that, after it has been all broken up, the further addition of acid is without effect. Maintaining the view that oxidation goes on mainly in the tissues around and not in the blood itself, Pflüger points out also (*Arch. f. d. Ges. Phys.* 1872, vi.) that, from what we know of the laws of gaseous diffusion, oxygen must pass, as such, from the blood into the neighbouring tissues, and carbonic anhydride in the opposite direction, and he shows that even asphyxiated blood, if it be examined quite fresh, contains an extremely small amount of reducing matters. In reference to this question Preyer has pointed out that it is almost certain that uncombined oxygen passes in the placenta from the maternal blood through the vascular walls into the foetal blood, and if such a passage of uncombined oxygen occurs in this tissue, there can be no doubt that it takes place in others also. Putting these facts together, it seems probable that most of the oxidation going on in the body occurs outside blood-vessels; but as to the rate at which it occurs in different tissues, or as to the stages of oxidation attained in each, we know but little. Bert (*Leçons sur la Phys. de la Resp.*, Paris, 1870) found that equal weights of different tissues, taken from an animal bled to death, took up different quantities of oxygen from blood. Arranged in order, beginning with those which take up most, the series runs—muscle, brain, kidney, spleen, testicle, and bone. A. Schmidt found that blood sent repeatedly through the vessels of fresh kidneys, kept at the body temperature, lost very rapidly nearly all its loosely held oxygen; no urine was secreted.

As to the matters which are burnt in the small oxidation which goes on normally in the blood almost as little is known. Beaumark compared the quantity of fat in blood, before it had passed through the lungs, with that in blood after passing through those organs: he found 0.1803 p.c. in the former, and 0.0062 p.c. in the latter, which also contained little or no fluid fats, while the former contained a considerable portion of them; from this he concludes that the fluid fats of the blood are oxidised in their circulation through the lungs. Schemenetjewski also (*Zeitschr. f. Biologie*, 1868, Dec.) has investigated the effect on the respiratory gases of the injection of combustible non-nitrogenated matters into the blood; he found that sodic lactate or caproate increased the quantity of oxygen taken up in the lungs and the quantity of carbonic anhydride given out, and J. J. Müller obtained the same results. Glycerin acted similarly but more rapidly, while sodic acetate and formate were without effect; grape-sugar sometimes increased the respiratory gas exchanges, but sometimes not, from which he concludes that it is not oxidised, as such, in the blood. It does not

indeed appear at all certain that any of these matters were oxidised in the blood itself.

With respect to the carbonic anhydride of the blood, considerable modifications will have to be introduced into the views which have hitherto prevailed, both as to its origin and state of combination. Until recently it has been very generally assumed, that it was contained wholly in the plasma and, in it, existed in three conditions, viz. dissolved simply, feebly combined, in the form of a double salt, with phosphate (Fernet's salt), and stably combined in the form of normal carbonates. Preyer (*Centr. f. d. Med. Wissen.* 1866) found that alkaline fluids, such as solutions of sodic carbonate or phosphate, or blood serum, or the urine of herbivora, all become acid or neutral when treated with carbonic anhydride, before such a quantity of the gas was added to them as to cause some of it to be simply in solution in the fluid; from this he concludes that the alkaline circulating blood can contain no simply dissolved carbonic anhydride, especially as it is known that fresh blood can combine with  $\text{CO}_2$  when exposed to it; he believes that those phenomena presented in the vacuum by blood, which have been taken to prove that it contains free  $\text{CO}_2$ , are really due to the development of acids by the decomposition of the hæmoglobin, which acids turn out carbonic anhydride from some of its compounds. In connection with this point Schöffer, Zuntz, and others have shown that an acid does not develop in the blood when it is removed from the body, and that its development is dependent on the presence of the red blood corpuscles. Now, if no free carbonic anhydride exists in the circulating blood, this must modify the view that another portion of this gas is combined in it in the form of Fernet's salt; for, as Hermann has shown, this salt can only exist in the presence of a certain tension of  $\text{CO}_2$ , which would not be exerted if none of it were present in the blood in an uncombined state; either, then, some carbonic anhydride exists in the blood in simple solution, or the view that a good deal of it is held in the form of Fernet's salt is incorrect. Hornmann inclines to the former opinion, but there is a good deal of evidence tending to show that the latter is the correct one. Sertoli (*Centr. f. d. Med. Wissen.* 1868, and *Med. Chem. Unters. v. Hoppe-Seyler*, 3 Heft.) found that the quantity of sodic phosphate which exists in the blood of oxen is extremely small. Laying aside the quantity of phosphoric acid which is combined with calcium in the blood, he found that almost all the rest, which had been previously considered as combined in the form of sodic phosphate, really belonged to the lecithin of the serum, which had been neglected by former observers; estimating the sodic phosphate as high as possible, he found that the quantity of carbonic anhydride which it could hold as Fernet's salt was not more than 0.75 vol. in 100 vols. of blood. The observations of other observers have at the same time shown that the red blood corpuscles are capable of combining with carbonic anhydride. Schmidt (1 *Abth. d. K. Sachs. Gesell.* 1867, and *Centr. f. d. Med. Wissen.* 1867) found that a part of the carbonic anhydride of the blood was stably combined with some body in the corpuscles, but that the quantity so combined was very variable, and greatly dependent on the amount of the gas obtainable from the plasma by the air-pump, and Zuntz, who has investigated the matter more thoroughly, confirms this (*Centr. f. d. Med. Wissen.* 1867, and *Beiträge 2 Phys. d. Blutes*, Bonn. 1868). He found that drawn blood exposed to a partial pressure of 8 p.c. of  $\text{CO}_2$  took up about its normal quantity of carbonic anhydride; under 10 p.c. partial pressure, the quantity taken up was disproportionately increased, and the excess was mainly held chemically bound by the corpuscles; which he therefore concludes to contain a body (perhaps the alkali-hæmoglobin of Pflüger) which is capable, under different partial pressures of carbonic anhydride, of combining with different quantities of that gas; under a partial pressure = 8 mm. of mercury, he finds the  $\text{CO}_2$  of the blood only to exist in the plasma (*Berl. Klin. Wochenschrift*, 1870, 186). From the mean of three analyses of the gases of normal blood, he concludes that 92 p.c. of its carbonic anhydride is chemically combined, 35.5 p.c. in the plasma, and 56.5 p.c. in the corpuscles. From Wolffburg's experiments (*Arch. f. d. Ges. Phys.* 1871 and 1872) it appears also that the tension of the carbonic anhydride in venous blood and in the air-cells of the lungs has been previously reckoned too high; he makes it equal to that in a gaseous mixture containing 3.6 p.c. of the gas, if this lower tension in the air-cells be correct, and if a great part of the carbonic anhydride of the blood exists in combination in the corpuscles, it becomes more easy than before to understand how the taking up of oxygen and the formation of ox hæmoglobin in the corpuscles during the pulmonary circulation is able to turn combined carbonic anhydride there into free, and so raise the tension of the gas sufficiently to enable it to diffuse into the air-cells in spite of the percentage of the gas in the air which they contain.

With regard to the source of the carbonic anhydride which is found in the blood, it is probable that a great part of it is not nearly so directly the result of oxidation as has been more or less definitely believed, but that a portion of it arises from the breaking up of more complex molecules without any necessary simultaneous oxidation;

such a process certainly appears to occur in the muscles (see *MUSCULAR TISSUE*), and J. J. Muller (*Bericht d. K. Sachs. Gesell. Wiss.* 1869) repeating, in a modified form, Schömann's experiments with sodic lactate, referred to above, finds that its introduction into the blood increases the quantity of carbonic anhydride expired, quite out of proportion to the extra quantity of oxygen taken up at the same time; he concludes that the lactate is not simply oxidised in the blood, but is broken up there, carbonic anhydride being one of the products. The origin of carbonic anhydride from such sources as these probably is the reason of the great difference between day and night with respect to the oxygen taken up and the carbonic anhydride given out during each, which Pettekofer and Voit found to exist. During the day the greater amount of muscular work going on develops a large amount of carbonic anhydride in the body, and so raises disproportionately the amount of the gas given off, as compared with night, when much less muscular work occurs, and more oxygen is taken up by the lungs than is expired in the carbonic anhydride. Liebermeister (*Arch. f. Klin. Med.* 1869. vii.) has also shown that the difference pointed out by Pettekofer & Voit is greatly dependent on the time of feeding.

Bert (*Compt. rend.* 1872) has made observations upon the effect of different atmospheric pressures on respiration; he found that birds breathing air under a pressure of 20 atmospheres died with convulsions and other symptoms, which he considers are due to oxygen poisoning; for if the pressure after these atmospheres was raised by nitrogen only, these symptoms did not appear. Rapid diminution of the pressure from seven atmospheres to one, killed animals either immediately or after a day or two, gases being set free from the blood within the blood-vessels. Analysis of the gas so set free showed that it contained 70-90 p.c. of nitrogen, the rest being carbonic anhydride.

H. N. M.

**RESTORMELITE.** A hydrated aluminium silicate from Restormel in Cornwall, exhibiting the characters of a decomposition-product of felspar. It is greenish-grey, amorphous, with a conchoidal fracture, and resembles agalmatolite in external appearance. When heated, it gives off water, and becomes grey and opaque. It does not gelatinise with sulphuric acid. Sp. gr. = 2.58. Hardness = 2. Its composition, according to the mean of six analyses, is:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O
45.66	35.09	1.18	0.85	2.30	4.39	11.68 = 101.15.

These numbers correspond pretty well with the formula of kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$  (46.3 p.c.  $\text{SiO}_2$ , 39.8  $\text{Al}_2\text{O}_3$ , 13.9 water), supposing the hydrogen to be partly replaced by sodium and potassium, and the aluminium by iron. Restormelite appears, however, to be an immature rather than an altered kaolinite (Church, *Chem. Soc. J.* [2], viii. 165).

**RHAMNETIN.** On the synthesis of this substance, the glucoside of rhamnetin, by boiling the lead-compound of rhamnetin with diacetyl-saccharose, see *GLUCOSIDES* (p. 567).

**RHINANTHIN**,  $\text{C}_{20}\text{H}_{32}\text{O}_{10}$ . This glucoside, which Ludwig obtained from the seeds of the common yellow rattle (*Rhinanthus Crista Galli*, 1st Suppl. 995), he has also prepared from those of *Alectrolophus hirsutus* (*Rhinanthus buccalis*, Wallroth). It crystallises in stellate groups of prisms; has a slightly bitter and nauseously sweet taste; dissolves easily in alcohol and in water. Its alcoholic solution mixed with hydrochloric acid, and heated, turns bluish-green, and decomposes. By dilute mineral acids it is resolved into a brown, non-crystallising substance called rhamnogenin, and a kind of sugar (H. Ludwig, *Arch. Pharm.* [2], cxlii. 199).

The seed of purple cow-wheat (*Melampyrum arvense*) yields to alcohol a chromo-glucoside, which in its reactions exhibits a close resemblance to rhinanthin (Ludwig & Müller, *ibid.* cxlii. 6).

**ROSDINNE.** The name given by Gladstone (*Chem. Soc. J.* [2], x. 3) to the hydrocarbon  $\text{C}_{10}\text{H}_{18}$  from rosewood oil.

**ROGADINE**,  $\text{C}_{17}\text{H}_{21}\text{NO}$  (1st Suppl. p. 995). This base may be regarded as dioxypapaverine (Hesse, *Ann. Ch. Pharm.* cliii. 47).

**RICININE.** According to E. Werner (*Chem. News*, xxii. 203) the constituent of castor-oil seeds, thus named by Tuson (v. 109) is not an alkaloid, but a magnesium salt having the composition  $\text{C}_{18}\text{H}_{31}\text{O}_4 \cdot \text{Mg} + 6\text{H}_2\text{O}$ . To this statement Tuson replies (*ibid.* 229) that the substance obtained by Werner is totally different from that designated by himself as ricinine, the latter containing 20.79 p.c. nitrogen and forming fine crystals.

**RICINUS OIL.** See CASTOR OIL (p. 270).

**BIONITE.** A bismuth fahl-ore occurring, together with heavy spar and quartz, at Cremenx in the Einfischthal (Val d'Anniviers) in the Canton Wallis. Analysis A is by Brauns, published by Petersen (*Jahrb. f. Mineralogie*, 1870, p. 464). The quantities of metal determined by this analysis require only 26.13 p.c. sulphur. Petersen himself found 26.87 sulphur, which he regards as too high, the excess arising from admixed copper-pyrites. Petersen therefore refers the analysis to the formula  $3\text{RS.RS}^*$ , which he regards as the typical formula of fahl-ores.

Petersen also gives an analysis (B), by R. Sontfer, of another bismuth fahl-ore from Neubulach in the Wurtemberg Schwarzwald. The mineral occurs in crude lumps, closely intergrown with the quartz matrix, one specimen only being crystallised in the combination  $\frac{\text{O}}{2} \cdot \frac{2\text{O}_2}{2} \cdot \infty \text{O}$ . Sp. gr. = 4.908.

S	As	Sb	Bi	Cu	Ag	Pb	Zn	Fe	Co	Ni	
29.10	11.44	2.19	13.07	37.52	0.04	—	—	6.51	1.20	—	= 101.07
24.85	13.63	4.28	6.33	41.43	trace	1.52	3.82	3.74	trace	trace	= 99.50

**BITTINGERITE** (v. 112, 1052). This mineral, from the Joachimsthal, has been re-examined by A. Schrauf (*Jahrb. f. Mineralogie*, 1872, 180). The small, many-faced monoclinic crystals are frequently twinned with the plane of combination parallel to  $0\text{P}$  or  $\infty \text{P}\infty$ . Sp. gr. = 5.63. It contains 57.7 p.c. silver, together with arsenic and a little selenium, but no sulphur.

**ROCKS.** On the chemical character and composition of certain Cornish rocks, see KILLAS (p. 713).

On the Permian rocks of the Lower Odenwald, see E. Cohen (*Jahrb. f. Mineralogie*, 1872, 98); *Chem. Soc. J.* [2], x, 796).

On the character of the crust produced upon terrestrial rocks by atmospheric agency, compared with the black coating of certain meteorites, see S. Meunier (*Compt. rend.* lxxv, 890; *Chem. Soc. J.* [2], xi, 141).

**ROMBIN.** From a recalculation of Damour's analysis of this mineral (v. 116) Kenngott (*Jahresb. f. Mineralogie*, 1870, 999) deduces the formula:



**ROOT-CROPS.** The principal root-crops cultivated by the farmer are:—Turnips, *Brassica Rapa* (Fr. *navet*, Ger. *Turnipsrübe*, *Weissrübe*); Swedes, *B. campestris*; Beet, *Beta vulgaris*, of which two main varieties, Mangel-wurzel (Fr. *betterave*, Ger. *Futterrunkelrübe*), and Sugar-beet (Fr. *betterave-à-sucre*, Ger. *Zuckerrübe*) are cultivated; Carrots, *Daucus Carota* (Fr. *carotte*, Ger. *Möhre*); and Parsnips, *Pastinaca sativa* (Fr. *panais*, Ger. *Pastinakwurzel*). These plants are all biennials, the first season being devoted to storing up matter in the root, and the second season to the production, out of the matter so accumulated, of a flowering stalk, and seed. As the root is in every case the part which is of economic importance, the attention of chemists has been concentrated upon the first period of the plant's life, and the second stage of growth has been little studied.

The composition of a cultivated root will depend—1. On its species; 2. On its size; 3. On its maturity, dependent upon its age and the climate it has been exposed to; 4. On the character of the soil and the manure employed. The differences of composition between various kinds of roots are shown in the table on p. 1049, which, except in the case of sugar-beet, gives the mean of all available analyses. The amount of variation among these analyses which yield the above means is, in most cases, very considerable; one cause is the distinctive characters of the different varieties of the same root; other circumstances which produce variations in composition will be considered presently.

The specific gravity of roots is generally less than that of their sap. Turnip root in water, Swedes of good quality sink. The sp. gr. of Swede sap is 1.016–1.024 (Murray). Sugar-beet sap rises sometimes to 1.08. The sp. gr. of sugar-beet roots rises and falls with that of the sap in the case of small roots, but with large roots discrepancies occur from the presence of air spaces.

The dry matter in fresh roots varies from 6–7 p.c. in some white turnips, to 21 p.c. in high quality sugar-beet. Roots begin to lose water as soon as they are pulled from the field; determinations of water are therefore frequently too low.



Average percentage Composition of Roots.

	Number of Analyses *	Water	Albuminoids	Fat	Extractive matter	Sugar	Cellulose	Ash
Turnips . . .	23	91.79	1.17	.20	1.85	3.22	1.08	.69
Swedes . . .	31	89.32	1.47	.20	2.06	5.25	1.10	.60
Mangels . . .	61	88.68	1.22	.10	1.45	6.23	1.32	1.10
Sugar-beet . . .	78	83.62	1.47	.10	2.43	10.10	1.42	.86
Carrots . . .	24	85.81	.97	.25	2.79	7.33	1.81	1.04
Parsnips . . .	2	85.17	1.44	.37	8.05	2.91	1.25?	.81

Average percentage Composition of Leaves.

Turnips . . .	27	86.60	2.71	—	8.93	—	—	1.76
Swedes . . .	26	85.00	3.78	—	9.47	—	—	1.75
Mangels . . .	15	90.93	1.74	.50	3.76	1.16	—	1.91
Sugar-beet . . .	12	88.80	2.32	—	4.16	1.90	—	2.82
Carrots . . .	2	79.35	3.51	1.14	9.33	3.22	—	3.45
Parsnips . . .	1	83.15	1.81	.40	9.88	2.17	—	2.50

The nitrogen in roots is by no means all in the form of albuminoids, though calculated as such in analyses; the figures given for albuminoids are therefore in every case too high. E. Schulze (*Landw. Versuchs-Stationen*, ix. 445; xv. 170) found in mangels 0.37–3.13 of nitric acid in 100 of dry substance; the mean of 21 specimens was 1.44 p.c. In the extreme case 31 p.c. of the nitrogen in the root existed as nitrates. Six kinds of turnips gave a mean of 0.276, and three specimens of carrots 0.189 p.c. of nitric acid in their dry substance. Frühling found, in the dry matter of the leaves of sugar-beet, 0.28–1.60 p.c. of nitric acid. Schulze has determined the ammonia in the sap of various roots; in mangels it varied from 0.0084–0.0223 p.c. of the fresh sap; the mean of eight examples was 0.0158 p.c.; in the sap of four carrots the mean was 0.0215 p.c. Ammonia is found in the condensed water from evaporating the juice of sugar-beet. According to Hesse, trimethylamine and ammonia are present in the sap of the leaves. Asparagine has been found by Scheibler in sugar-beet, and is probably generally present in roots in small quantity; in sugar-beet which had been stored Scheibler found aspartic acid. Betaine, the nitrogenous base discovered by Scheibler in the sap of sugar-beet, has been already described (see *BETAINES*, 1st Suppl. 340; 2nd Suppl. 186); the percentage of betaine in the sap diminishes as the root matures. Scheibler found .234 p.c. in the sap on July 1, and .084 p.c. on October 1. In the molasses of the sugar-beet factories the betaine reaches 1.59–2.78 p.c. The nature of the albuminoids in roots has not been thoroughly investigated; they appear to contain both legumin and albumin. In sugar-beet the cambium is said to be the part of the root richest in albuminoids. In parsnips Voelckor found that the intermediate layer separating the heart from the exterior was by much the most nitrogenous.

The fatty matter of roots has not been especially investigated; according to König the fat in beet-root is chiefly concentrated in the rind. The fat mentioned in the analyses as present in the leaves doubtless includes chlorophyll.

Sugar is one of the most important constituents of cultivated roots, and upon it their feeding value greatly depends. In the case of sugar-beet, by careful selection of seed and appropriate cultivation, the proportion of sugar has been raised to 13–14 p.c. for small roots, and under exceptional circumstances much higher quantities are obtained; according to Vilmorin 21 p.c. has actually been reached in some cases. Sugar is not uniformly distributed in beet-root; the cellular tissue which lies in contact with the cambium is the richest. The top of the root is always poor in sugar; the proportion, according to Viollette, increases regularly downwards. Sebor, however, found the extremity poorer than the centre. The sugar in beet-root is almost entirely saccharose, only a very small quantity of glucose and levulose being present; this quantity increases, however, when the roots are stored, especially, according to Pasteur, if

\* These numbers refer to analyses in which water, nitrogen, and ash have all been determined; determinations of fat, cellulose, and sugar are in most cases much lower. Where isolated determinations have been introduced, they have been recalculated so as to accord with the mean dry matter. Thus the sugar in Swedes is the mean of 4 determinations by Sullivan. He found 7.26 p.c.; but the dry matter in his roots, which had been exposed some weeks, was 14.75 p.c.; the sugar therefore in 100 of dry matter is 6.26.

the heap of roots is ill-ventilated, and carbonic acid is allowed to accumulate. The sugar in the leaf and leaf-stalk of sugar-beet is, according to Méhay (*Jahresb. Agri. Chem.* 1868-9, 278), almost entirely uncrystallisable. In carrots a large proportion of the sugar is, according to Dietrich, in the form of glucose (fructose, Brotschneider); mannite has also been found in this root.

Starch has not been recognised in turnips or Swedes; in unripe sugar-beet a small quantity has occasionally been found by Sullivan, which disappeared as the root matured. In wild carrots starch is abundant; in cultivated carrots the quantity is much diminished, and may apparently disappear altogether, being probably replaced by sugar. Karsten found 6·8 p.c. of starch in carrots; Voelcker found none. Parsnips also contain starch; Voelcker found 3·5 p.c. in the fresh root. In both carrots and parsnips the starch is deposited next the rind; the internal parts of the parsnip, according to Voelcker, contain no starch.

The insoluble fibrous matter of roots, which forms the substance of the mark when roots are pressed, consists of cellulose, a small quantity of lignose (suberin), which constitutes the cuticle of the root, and a more or less considerable amount of pectose. Scheibler (*Deut. Chem. Ges. Ber.* vi. 612) has also shown that in the sugar-beet of some seasons a considerable amount of insoluble arabin (metarabin) is present. The arabin appears to consist of two bodies—the principal, a powerfully levorotatory substance, yielding arabinose, a right-handed crystalline sugar, when acted on by dilute sulphuric acid; the other, a closely allied body, apparently dextrorotatory, which, on treatment with sulphuric acid, yields a non-crystalline sugar. These bodies have not yet been separated. Only a few determinations of cellulose have been made in roots, the crude fibre being generally weighed without previous separation of the pectose; both pectose and metarabin may be removed by boiling the crude fibre with an alkali.

H. Schultze a. E. Schulze (*Landw. Versuchs-Stationen*, ix. 439) have made ultimate analyses of the mark of roots from which all matter soluble in cold water had been removed; in the case of carrots the mark was previously treated with malt-extract to remove the starch.

	Composition of Mark					Mark after deducting albuminoids and ash		
	C	H	O	N	Ash	C	H	O
Mangel, unripe	44·80	6·11	45·07	1·21	2·81	45·50	6·22	48·28
Mangel, after wintering	44·92	5·92	46·21	·73	2·22	45·69	6·01	48·40
Carrot, after wintering	43·34	5·78	46·53	1·19	3·16	44·07	5·80	50·04

The numbers for the pure carbo-hydrate differ little from the composition of cellulose; the differences in the first two analyses are in the direction of lignose, and in the last in the direction of pectin. It is evident in the case of mangels that the insoluble albuminoids and ash found in the mark diminish as the root matures.

The mark obtained from beet-root in the sugar-factories on the continent is largely consumed as a cattle-food; the average composition of the residua obtained by the old process of pressure, and by the newer and more effective plan of diffusion, is about as follows:

	Water	Albuminoids	Fat	Sugar	Extractive matter	Cellulose	Ash
Press residue	70·00	1·84	0·20	3·00	16·83	5·13	3·00
Diffusion residue	91·62	0·67	0·07	6·30	4·75	1·75	0·64

The diffusion residue contains in the dry more albuminoid than the press residue; the large amount of ash is owing to the earth adhering to the roots.

Of the organic acids present in roots, oxalic acid is the most important; it is present in mangel and sugar-beet, and reaches a high percentage in their leaves. The sap of sugar-beet, according to Michaelis, contains '08 p.c. of oxalic acid, and '11 p.c.

of citric acid; this oxalic acid is, of course, in a soluble form. The total oxalic acid in the root of sugar-beet was found by Méhay to be 22 p.c.; the leaf-stalk of the same roots contained 43 p.c., and the leaves 1.86 p.c. A. Müller puts the oxalic acid in mangel leaves at 2 p.c., with citric and malic acid 15 p.c. Mittenzwey has shown (*Landw. Versuchs-Stationen*, i. 242) that the different circles of mangel leaves contain very different amounts of oxalic acid; the innermost youngest leaves gave 1.85 p.c. of oxalic acid in their dry matter; the outermost oldest leaves 10.98 p.c.; the percentage rose regularly from the innermost to the outermost leaves. About two-thirds of the acid existed pretty uniformly in an insoluble state. Cattle are occasionally poisoned by eating the leaves of mangel. Oxalic and tartaric acids have been mentioned as present in turnip leaves; carrots are said to contain malic acid.

The colouring matters of roots do not appear to have been investigated, save in the case of carrots (see CAROTIN, i. 805).

Ultimate analyses of the whole substance of turnips and mangels have been made by Boussingault, and by Richardson (*Jour. Roy. Agri. Soc.* xiii. 458), and ultimate analyses of mangels and carrots by H. Schultze (*Landw. Versuchs-Stationen*, ix. 439).

The average composition of the ash, both of roots and leaves, is shown in the following table; the figures are the mean of nearly all the available analyses. The percentage composition has been calculated after deduction of carbonic acid, but the amount of carbonic acid in the original ash is also given as far as it could be ascertained; in the German analyses it is usually omitted.

*Average Composition of the Ash of Roots, Carbonic Acid deducted.*

	Number of analyses	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>2</sup>	Cl	SiO <sup>2</sup>	CO <sup>2</sup> in original ash
Turnips . . .	38	49.8	7.8	11.7	2.6	.9	10.3	11.8	5.0	1.2	14.0
Swedes . . .	7	38.9	14.0	12.8	4.2	.8	10.4	13.7	4.2	1.9	12.9
Mangels . . .	12	46.6	18.4	5.9	4.8	.8	8.3	3.7	9.9	4.0	19.0
Sugar-beet . .	40	48.0	10.4	6.4	9.5	1.0	14.4	4.7	2.3	3.8	13.7
Carrots . . .	10	37.0	20.7	10.9	6.2	1.0	11.2	6.9	4.9	2.0	17.9
Parsnips . . .	4	46.7	2.7	15.7	6.0	1.3	15.8	5.6	4.0	2.4	14.5
<i>Leaf Ash, Carbonic Acid deducted.</i>											
Turnips . . .	37	27.6	5.1	33.2	2.6	2.0	7.3	13.1	7.7	3.6	12.7
Swedes . . .	3	21.0	12.3	30.2	3.2	2.0	6.4	10.6	11.0	4.8	8.4
Mangels . . .	4	25.5	23.3	10.4	9.7	1.2	6.4	7.2	17.8	3.3	14.5
Sugar-beet . .	7	21.9	16.6	19.5	18.1	1.3	7.3	7.9	5.7	3.1	—
Carrots . . .	7	17.6	18.2	32.1	3.9	3.0	3.8	8.2	8.9	5.2	10.1

The range of variation in these analyses is, in every case, very great. The most constant ingredients in the ash of roots are those most essential to plant-life, potash and phosphoric acid; the most variable constituents are soda and chlorine. The variations in the ash-constituents of the leaves are even greater than in the case of roots.

The ashes of all the roots are, on the whole, of similar character. The ashes of the Brassicæ are particularly rich in sulphates, both in root and leaf. The ash of mangel and of sugar-beet differ from each other considerably in some points, though the plants are the same species. In cultivating sugar-beet the aim is to obtain roots with a small amount of ash, as saline matter prevents the crystallisation of the sugar, and to this end small roots, scantily manured, are produced; mangel is, on the other hand, cultivated with a view to bulk. The small ash of the sugar-beet is of a concentrated nature, rich in potash, phosphoric acid and magnesia. The large ash of the mangel are apparent, but in this case the large amount of lime in sugar-beet is probably due to the greater maturity of the plant when harvested. Peligot remarks that beet is one of the plants in which soda is always found abundantly, while parsnips are destitute of soda; and this difference is maintained even when beet-root and parsnips are cultivated in the same bed. Rubidium occurs in minute quantity in the beet-root of the north of France, and may be obtained from the ash of the residue which remains after distill-

ing the fermented molasses. According to Lefebvre, the amount of rubidium chloride in an average crop of sugar-beet is 224 grams per hectare; Pfeiffer estimates the quantity at 255 grams. A trace of cesium, and small quantities of iodine and bromine, but no lithium, were found by Pfeiffer in the same ash. Manganese has also been recognised in the ash of sugar-beet.

The ash of the leaves is seen to have a very different composition from that of the roots, the potash and phosphoric acid being much smaller, and the lime and chlorine far greater. In connection with the large amount of chlorides in the leaves, Peligot and Viollette have observed that the chlorides in the root of sugar-beet are most abundant at the neck, and decrease from this point downwards.

The amount of carbonic acid in all these ashes should correspond with the combined amounts of organic salts and nitrates present; the various temperatures, however, at which the ashes have been burnt, prevent any stress being laid on the figures given in the table.

Having described the general composition of the various plants grown as root-crops, we turn to the circumstances which modify this composition. Luxuriantly growing plants always contain more water, and, as a rule, more nitrogen and ash, than less vigorous plants of the same age; this is true of roots, and consequently large roots and small ones, taken at the same time from the same field, exhibit considerable differences in composition. The following comparative analyses by different chemists will illustrate this point.

	Water	Nitrogenous matter	Sugar	Extractive matter	Crude fibre	Ash
Mangel, 9 lbs. .	91.85	1.34	2.86 3.95	2.54 4.51	1.41 0.82	
" 7½ lbs. .	89.48	1.24				
Mangel, 4 lbs. .	89.77	0.73	7.68 10.51	0.89 1.07	0.93 0.91	
" 1-2 lbs. .	86.90	0.61				
Sugar-beet, 5½ lbs. .	88.01	2.08	5.60	1.93	2.38	1.10
" 1½ lbs. .	84.35	1.17	8.10	5.28		

It is evident from these facts that small roots will always contain a larger proportion of nutritive matter than large roots of the same age. The feeding power of a crop is thus not necessarily in proportion to its weight; the more bulky the crop the smaller is the proportion of solid matter it contains. The differences of composition due to the size of the root are more strikingly seen in the case of beet than with other root crops. Small mangolds approach sugar-beet in composition; over-grown sugar-beets are quite similar to mangels. To obtain sugar-beet of the highest quality it is well known that the roots must not exceed 2 lbs. in weight.

One reason of the difference between large roots and small ones of the same age is that the more bulky root is less mature than the small one; this brings us to the next point, the effect of age on the composition of root-crops. The composition of the turnip plant in different stages of growth has been investigated by Anderson (*Trans. Highland Soc.* 1860, 307, 360), and by Wunder (*Jahresb. Agri. Chem.* 1861-2, 74, 107). Mangel-wurzel has been investigated by Wolff (*ibid.* 1860-1, 139), and its leaves by A. Müller and Mittenswey (*Landw. Versuchs-Stationen*, i. 241). Sugar-beet has been studied during its first stage of growth by Bretschneider (*Jahresb. Agri. Chem.* 1860-1, 129; 1861-2, 88, 261), Hoffmann (*ibid.* 1862-3, 119), Eylarts (*ibid.* 128), Nobbe a. Siegert (*ibid.* 69), Scheibler (*ibid.* 1870-2, iii. 286), Lotmann (*ibid.* 287), and Church (*Trans. High. Agri. Soc.* [4], iv. 85). The changes in its ssp. have been observed by Hoffmann (*Jahresb. Agri. Chem.* 1860-1, 132; 1861-2, 83), and Méhay (*ibid.* 1870-2, iii. 285). The second period of growth, in which seed is produced, has been studied by Hoffmann (*ibid.* 1861-2, 87), and by Corenwinder (*ibid.* 1867, 126). Carrots have been investigated by Bretschneider (*ibid.* 1861-2, 101).

In the life of all root-crops the leaf is the part which is at first most actively developed, but as growth proceeds the proportion of root to leaf steadily increases. When active growth comes to an end the older leaves wither and fall off, a considerable part of their constituents being transferred to the root. Anderson's research on turnips will serve to illustrate the general relation of leaf to root, and at the same time supply information on the turnip crop. The crop amounted to 16 tons of roots per acre; it was heavily manured.

*Composition of a Turnip Crop at various periods in lbs. per acre.*

	July 7		August 11		September 1		October 5	
	Leaf	Root	Leaf	Root	Leaf	Root	Leaf	Root
Organic matter . . .	16.13	1.16	990	190	1720	1293	1084	2762
Ash . . . . .	1.36	.24	239	25	374	148	210	734
Dry matter . . . .	17.49	1.40	1233	215	2094	1441	1294	3496
Potash . . . . .	0.14	0.05	41.2	8.0	87.2	43.1	32.6	205.6
Soda . . . . .	0.09	0.02	21.2	3.5	30.5	14.4	19.0	87.3
Lime . . . . .	0.30	0.03	34.9	2.1	48.8	12.0	14.2	88.0
Magnesia . . . . .	0.08	0.02	16.7	1.0	27.6	5.9	28.9	36.4
Ferric oxide . . . .	0.07	0.01	6.9	0.6	8.4	2.0	5.0	10.1
Phosphoric acid . . .	0.15	0.03	20.1	3.0	39.1	16.4	23.8	74.5
Sulphuric acid . . .	0.13	0.02	37.4	2.3	48.2	24.6	20.4	95.8
Chlorine . . . . .	0.10	0.01	16.7	1.2	34.8	8.0	22.7	42.5
Silica . . . . .	0.01	0.02	7.2	.6	10.3	4.5	7.5	22.8

On July 7 the dry matter of the root was to that of the leaf as 8 : 100; on October 5 the proportion was 270 : 100.

The results of Wunder and of Anderson in their three series of experiments with turnips are somewhat discordant; we will therefore mention only some general facts.

As a rule the composition of a root-crop undergoes the following changes. In the seedling the proportion of dry matter is at its maximum; the water, in both root and leaf, afterwards increases up to the period of most active growth, but as the plant matures the water again diminishes. In the case of turnips the increase of dry matter in the root during the latter part of its growth is but little marked, and is apparently confined to the latest stage. The nitrogen in the dry matter is also at its maximum in the seedling (Anderson and Wunder both found 5-6 p.c. of nitrogen in seedling turnips), and falls afterwards both in root and leaf. With turnip-roots the nitrogen appears to rise after the first fall until the last stage is reached, when the amount again diminishes. The amount of ash in the dry matter of the root tends to diminish as the plant matures. With turnip-root the ash, after falling, rose in all cases during the final stage of growth. The proportion of ash in the dry matter of the leaves is often more constant than in the root; in the case of turnip-leaf the ash appears to diminish as the plant matures; probably, however, rising again when withering commences. The maximum content in nitrogen generally occurs very early in a plant's life, the maximum contents in water and ash generally coincide with the period of most active growth.

The relative proportion of the ash-constituents, as shown in the composition of the ash per cent., varies during the growth of the turnip as follows. In leaf and root there is in the first case a rise in potash, which, in the case of the root, is very considerable, and a corresponding fall in lime and magnesia. The potash in the leaf generally diminishes somewhat in the last stage of growth, the other bases rising. Chlorides increase steadily in the leaf throughout its growth. At the end of the growing time the root-ash is richer both in potash and phosphoric acid than at the beginning, and poorer in lime and magnesia; the last-named bases rise somewhat in the final stage of growth. The changes in the leaf-ash are more irregular.

In Bretschneider's experiments with carrots the alterations in composition were very regular. His experiments did not commence with the seedling; the great changes which usually occur in the primary stage were therefore not observed. In the leaf the dry matter was at its minimum (11.61 p.c.) on August 14, and then rose steadily to 17.72 p.c. on October 10. The dry matter of the root slowly increased from the first, and, with but one irregularity, reached its maximum at the end of the experiment. The amounts of nitrogen and ash in the dry matter of the root regularly diminished. The dry matter in the root was to that in the leaf as 34 : 100 on July 25, and rose to 87 : 100 at the close of the experiment. Bretschneider's analyses of the carrot-root in various stages are very typical of the changes which usually take place in root-crops; his results were as follows:

	Carrot-root, fresh					Carrot-root, dry				
	July 25	Aug. 14	Sept. 4	Sept. 19	Oct. 10	July 25	Aug. 14	Sept. 4	Sept. 19	Oct. 10
Water	90.58	90.20	89.95	90.47	89.24	—	—	—	—	—
Albuminoids	1.10	1.00	1.03	.83	.73	11.67	10.20	10.24	8.71	6.78
Extractive matter	2.34	2.11	1.89	1.95	2.10	24.84	21.53	18.80	20.46	19.51
Cane-sugar	1.17	1.04	1.30	1.35	2.49	12.42	10.61	12.94	14.17	23.14
Fruit-sugar	8.18	3.65	3.91	3.63	3.59	33.23	37.25	38.91	38.09	33.37
Fibre	1.07	1.31	1.29	1.20	1.20	11.36	13.37	12.84	12.59	11.16
Ash	0.61	0.69	0.63	0.57	0.65	6.48	7.04	6.27	5.98	6.04

The total sugar in the dry matter steadily increases, but at first it is the fruit-sugar which rises, and afterwards the cane-sugar. The fibre comes to a maximum early in the growth, and then diminishes.

The ash-analyses of the carrot-root and leaf exhibited little variation during the experiment; the percentage composition of the ash (carbonic acid deducted) was in the first and last stages as follows:—

	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	Cl	SiO <sup>2</sup>
Leaf, July 25	18.12	30.80	20.89	7.67	1.23	7.30	7.26	5.07	2.80
„ Oct. 10	14.68	28.70	27.45	6.70	1.86	6.38	9.72	2.71	2.40
Root, July 25	28.67	34.67	8.75	5.72	0.39	13.19	4.44	2.55	2.19
„ Oct. 10	30.48	28.88	11.53	6.46	0.40	14.99	3.49	2.08	2.08

In the case of sugar-beet, the alteration in the composition of the root during growth is far more striking than in the preceding instances; the following are Bretschneider's results. His experiment, as in the case of carrots, did not commence at the youngest stage. The proportion of the dry matter in the root to that in the leaf was at the commencement, on July 20, 61 : 100; it had risen by October 16 to 417 : 100.

	Sugar-beet roots, fresh						Sugar-beet roots, dry					
	July 20	Aug. 9	Aug. 31	Sept. 15	Sept. 30	Oct. 16	July 20	Aug. 9	Aug. 31	Sept. 15	Sept. 30	Oct. 16
Water	88.78	88.99	86.62	85.46	82.19	82.19	—	—	—	—	—	—
Albuminoids	2.08	2.35	2.01	2.13	2.48	2.28	18.61	18.67	15.06	14.74	13.92	12.84
Extractive matter	2.61	1.67	1.66	1.30	1.53	1.85	23.12	17.86	11.61	8.92	8.01	10.10
Cane-sugar	4.54	5.15	7.81	9.17	11.81	11.00	40.46	46.77	58.37	62.98	66.31	66.81
Fibre	1.17	1.09	1.01	1.21	1.22	1.10	10.50	9.89	8.30	8.34	7.43	6.42
Ash	0.82	0.75	0.89	0.73	0.77	0.68	7.31	6.81	6.66	5.02	4.33	3.83

We see that after August 9 the beet-root increased rapidly in dry matter, and that this increase was practically an increase of sugar, the composition of the dry substance showing a regular fall in nitrogen, ash, fibre, and extractive matter, and a corresponding rise in cane-sugar. The sap, forming as it does the mass of the root, undergoes a similar change. Sugar-beet, when harvested, contains about 4 p.c. of insoluble matter; the rest is sap. The proportion of ash and nitrogen in the sap falls considerably in the earliest stages of growth, and then remains tolerably constant; the sugar, however, continues to increase; the relation, therefore, of the soluble impurities (*Nichtzucker*) to the sugar steadily diminishes. Thus in Scheibler's experiments the sap contained, on July 1, 66.01 of soluble impurity for 100 of sugar; but on October 1 the proportion

had become 12.89 : 100, and the percentage of sugar in the dry matter of the sap (*Zuckerquotient*) had increased from 64.1 to 88.6. This is, of course, the view of the question specially regarded by the sugar manufacturer.

In Bretschneider's investigation the alteration in the composition of the leaf was as follows:

	Sugar-beet leaf, fresh						Sugar-beet leaf, dry					
	July 20	Aug. 9	Aug. 31	Sept. 15	Sept. 30	Oct. 16	July 20	Aug. 9	Aug. 31	Sept. 15	Sept. 30	Oct. 16
Water . . .	88.78	90.50	90.28	87.33	86.92	79.31	—	—	—	—	—	—
Albuminoids	3.16	2.81	2.03	2.58	2.60	3.95	28.04	29.56	20.89	20.38	19.88	19.12
Extractive matter	4.42	3.54	4.48	5.88	6.35	8.92	39.46	37.32	46.10	46.39	48.56	43.09
Fibre . . .	1.46	1.51	1.40	1.95	2.06	3.98	13.00	15.86	15.32	16.39	15.73	19.24
Ash . . .	2.19	1.64	1.72	2.26	2.07	3.84	19.50	17.26	17.69	17.84	15.83	18.55

August 9 is, as in the case of the root, the date from which the increase in dry matter commences. The proportion of nitrogen in the dry matter is seen to diminish rapidly at first, and afterwards to be but slightly altered. The ash after falling rises again at the last. A rise in the incombustible matter of leaves always takes place when withering has commenced. A Müller found 30 p.c. of ash in the dry matter of yellow mangel-leaves collected in August, while green leaves collected on the same day gave 17 p.c. The withered leaves contained also less water. The extractive matter in the analyses includes sugar; it therefore rises, instead of falling, as in the root.

The changes which take place in the leaves of a root-crop are much complicated by the fact that new and old leaves are very dissimilar in composition. Bretschneider examined separately the different circles of leaves formed by sugar-beet. The youngest, innermost leaves contained 10.88 p.c. of dry matter, and this dry matter contained 8.35 p.c. of ash. The amount both of water and ash steadily increased from the centre outwards, till the 6th, outermost circle of leaves, which contained 8.91 p.c. of dry matter, and 15.98 p.c. of ash in the dry. Mittenzwey found a yet wider variation among mangel leaves, the innermost giving 12.01 p.c. of dry substance, and 14.3 p.c. of ash in dry, and the 7th outermost circle 8.64 p.c. of dry matter, and 31.16 p.c. ash in dry. His interesting results as to the increase of oxalic acid from the youngest leaves to the oldest have been already mentioned.

Bretschneider made complete analyses of the ash of the root and leaf of sugar-beet at each of the periods mentioned above, and also on another occasion analysed the ash of the different circles of sugar-beet leaves. The following selection will give some idea of his results:

	K <sup>2</sup> O	Na <sup>2</sup> O	CaO	MgO	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	Cl	SiO <sup>2</sup>
Root, July 20 . . .	48.00	14.25	3.44	7.89	.73	15.99	4.22	2.76	3.34
" Oct. 16 . . .	44.08	5.78	6.46	10.48	1.15	17.85	8.89	2.97	3.06
Leaf, July 20 . . .	17.75	18.19	12.04	25.93	1.65	10.38	4.89	9.73	1.65
" Oct. 16 . . .	22.62	12.86	18.20	16.46	1.21	9.17	8.34	7.20	5.58
Leaf, innermost . .	50.27	14.57	4.76	6.71	0.51	12.69	5.86	3.97	1.56
" outermost . . .	18.74	18.26	24.20	24.48	1.42	3.30	5.37	3.50	1.52

The alterations brought about by age are on the whole similar to those observed in the case of carrots (see above); the large increase of lime in both leaf and root is in all cases a marked feature. Bretschneider remarks that the sugar contents of the root is greater the smaller is the proportion of the alkalis to the alkaline earths; the diminution of this proportion is, in fact, an indication of an advancing maturity. The same rise in lime was also observed in some of the investigations on turnips. The difference between the ash of the youngest and oldest leaf, existing together on the same plant, is seen to be far greater than that between the total leaves gathered at remote periods.

The different circles of leaves in beet-root are in connection with corresponding

cylindrical layers of the root. The plant grows by producing first fresh leaves, which form a new innermost circle, and from these leaves a new exterior layer of the root takes its rise. The function of new leaves is thus to increase the size of the root; the function of the mature leaves is to store up matter in the root layers already formed. In experiments by Schacht it appeared that removing full-grown leaves did not necessarily lessen the weight of the root at harvest, but it considerably diminished the proportion of sugar. The composition of the ash of the youngest leaves is seen to be of the most concentrated character, rich in potash and phosphoric acid, and corresponds with their function of producing new tissue. Bretschneider separated the various layers of beet-root and examined them separately; his results have unfortunately not been published in the *Jahresbericht*.

The changes in mangel-wurzel during growth should be similar to those in sugar-beet; the crop, however, being always highly manured, the period of active growth is long continued, and the increase of dry matter and sugar which should take place during ripening occurs to only a small extent.

When roots are taken from the field and stored for future consumption, they slowly lose in weight, carbonic acid and water being evolved. The quality of the root for feeding purposes is, in the case of mangel, much improved by wintering, but the precise nature of the change has not yet been investigated.

The changes which occur during the second year of the life of a root crop have been investigated only in the case of sugar-beet. The fresh development of leaves in the spring is accompanied by a considerable diminution of sugar, but after this point the amount of sugar remains unchanged until the formation of seed commences. When the seed is ripe, the root is found to be destitute of sugar, and also to have lost the whole of its phosphoric acid. A large increase of nitrates in the root takes place during the formation of seed; the nitrates disappear as the seed ripens. A root which had produced ripe seed contained, according to Corenwinder, water 90.35, cellulose 2.95, pectose and extractive matter 4.58, ash 2.12 p.c. When, however, as sometimes happens, a sugar-beet runs to seed in the first year of its life, the alterations are much less marked. The production of seed being less vigorous, the root retains a considerable amount of sugar (½ths, according to Church); it contains, however, more cellulose, ash, and less phosphoric acid.

The seeds of root-crops have been little examined. For ash-analyses of mangel, turnip, and carrot seed, see vol. i., pp. 583, 655, 807.

We have now to consider the last condition affecting the composition of root-crops—the influence of soil and manure. The effect of the composition of the soil, both on the bulk and composition of root-crops, is best illustrated by the results obtained at Rothamsted. Mr. Lawes' experimental field has grown roots since 1843, and similar manures having been applied every year to the same plots, the conditions of the soil have become very distinct. The following selection of unpublished results relating to turnips, swedes, and sugar-beet has been kindly communicated by Messrs. Lawes and Gilbert.

*White Turnips, average Produce and Composition, 1847-8.*

Manures	Produce, cwt. per acre		Leaf to 100 root	Dry matter per cent.		Ash in dry per cent.		Nitrogen in dry per cent.	
	Root	Leaf		Root	Leaf	Root	Leaf	Root	Leaf
Unmanured . . . . .	36	25	69	9.1	14.3	7.3	14.1	—	—
Ammonium salts . . . . .	40	20	50	9.2	15.0	7.6	14.1	—	—
Ditto, and rape-cake . . . . .	165	118	72	8.3	13.0	8.1	11.3	—	—
Superphosphate . . . . .	160	49	31	8.7	14.6	7.1	11.6	—	—
Ditto, with ammonium salts . . . . .	208	93	45	7.7	13.7	8.5	10.9	—	—
Ditto, ditto, with rape-cake . . . . .	228	168	60	7.7	12.6	8.9	10.2	—	—
Superphosphate and alkali salts . . . . .	165	48	29	8.4	14.0	7.4	11.9	1.63	3.00
Ditto, with ammonium salts . . . . .	240	81	34	8.3	13.4	8.0	11.4	2.47	3.37
Ditto, ditto, with rape-cake . . . . .	264	150	57	7.6	12.3	9.1	11.6	2.49	—



# ROOT-CROPS.

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*Swedes, average Produce and Composition, 1840-52.*

Manures	Produce, cwts. per acre		Leaf to 100 root	Dry matter per cent.		Ash in dry per cent.		Nitrogen in dry per cent.	
	Root	Leaf		Root	Leaf	Root	Leaf	Root	Leaf
Unmanured . . . . .	46	6	13	11.4	17.1	4.4	12.2	—	—
Ammonium salts . . . . .	79	6	8	11.3	18.0	4.5	11.6	—	—
Ditto, and rape-cake . . . . .	140	17	12	10.8	18.9	4.3	11.6	—	—
Superphosphate . . . . .	149	11	7	11.4	17.0	4.0	11.6	1.44	4.11
Ditto, with ammonium salts . . . . .	169	13	8	11.3	17.1	4.0	12.4	1.90	4.08
Ditto, ditto, with rape-cake . . . . .	224	21	9	10.6	15.8	4.2	10.6	2.30	4.16
Superphosphate and alkali salts . . . . .	157	10	6	11.0	16.1	4.6	12.8	1.38	3.87
Ditto, with ammonium salts . . . . .	189	11	6	11.8	18.3	4.7	12.3	1.59	4.06
Ditto, ditto, with rape-cake . . . . .	261	18	7	10.6	17.6	5.1	12.6	2.14	4.08

*Sugar-Beet, average Produce and Composition, 1871-3.*

Manures	Produce, cwts. per acre		Leaf to 100 root	Dry matter per cent.		Ash in dry per cent.		Sugar in root per cent.
	Root	Leaf		Root	Leaf	Root	Leaf	
Superphosphate . . . . .	118	29	25	18.7	12.5	3.0	23.0	13.8
Ditto, with ammonium salts . . . . .	270	90	67	17.6	9.6	4.2	24.0	12.5
Ditto, with sodium nitrate . . . . .	301	104	27	16.4	9.8	5.1	23.2	11.3
Superphosphate and alkali salts . . . . .	129	29	22	18.0	12.0	4.1	23.6	13.7
Ditto, with ammonium salts . . . . .	303	67	22	18.6	11.3	4.7	23.9	12.8
Ditto, with sodium nitrate . . . . .	305	113	29	16.8	9.9	5.2	22.2	11.7
Farmyard manure . . . . .	326	86	26	17.5	10.6	5.0	23.3	12.5

We must first look at the proportion of leaf to root at the time of harvest. Other things being equal, a low proportion of leaf to root signifies, as we have already seen, maturity in the root, while a high proportion shows that the crop is still in a growing condition. Looking at the character of the white turnips manured by superphosphate alone, and with various nitrogenous manures in addition, we see that each increase in the amount of nitrogen is followed by a large increase in the proportion of leaf, and consequently by a less matured produce. The composition of the turnips varies in the same direction. In the less mature crops the percentage of dry matter falls in both root and leaf, and the percentage of ash and nitrogen in the dry matter of the root rises. The effect of the manures is here perfectly consistent with the facts previously mentioned. The addition of nitrogen to phosphatic manure produces larger roots and a prolonged period of active growth, and is attended with the same alteration in composition of the crop as we have already seen accompany increase of size and deficient maturity. In the case of Swedes the changes produced by the addition of nitrogen to superphosphate are in the same direction as with turnips, but the alterations in the proportion of leaf, and in the ash, are less conspicuous. With sugar-beet the changes in composition, with a similar series of manures, are very well marked; the percentage of sugar clearly follows the other signs of maturity.

Besides these general facts, the tables show us that where alkalis (in these experiments, sulphates of potassium, sodium, and magnesium) are employed, the amount of leaf is always much less, and the proportion of ash in the produce greater. The effect of alkalis on the leaf explains the anomalous proportion of leaf in the sugar-beet manured with sodium nitrate in the first series. In the second series in the table all the plots receive alkalis, and in this case the lesser maturity of the beet grown with sodium nitrate is correctly shown by the larger proportion of leaf.

The unmanured turnips have a distinct character from those hitherto considered: with a large proportion of leaf, they have also a very high dry matter, and a comparatively low ash. In this case the crop is so small that no active growth can have taken place; the root thus remains with a low percentage of water, though still immature. For the same reason these diminutive roots are very rich in nitrogen. We have already remarked that the turnip seedling contains 5-6 p.c. of nitrogen in its dry matter, and that this high percentage diminishes as soon as active growth sets in. In 1846 the nitrogen was determined in the unmanured white turnips, which that year weighed less than 2 ozs. a piece; it amounted to 3.31 p.c. of the dry matter, a greater proportion than was yielded by any of the manured turnips.

The tables show that the composition of the leaf is less affected by manuring than the root. The percentage of nitrogen in the leaf remains very constant, and the variations in the ash are on the whole less.

We see from these experiments, that when turnips are grown with superphosphate only, the crop comes early to maturity; and that when nitrogenous manures are added to the superphosphate, the crop at the end of the autumn is less mature, and contains a smaller amount of dry matter, and more ash and nitrogen. For the reason, however, that growth is not concluded, the latter crop is better able to withstand the effect of frost.

The feeding value of turnips is by no means in proportion to their contents in nitrogen. In 1848 Mr. Lawes determined, by experiments with sheep, the feeding value of four lots of white turnips from the experimental field; the percentage composition of the turnip and the result of the trial were as follow:—

	Nature of manuring			
	Cinereals only	Cinereals with ammonia	Cinereals with rape-cake	Cinereals, ammonia, and rape-cake
Dry matter in fresh . . . .	9.37	8.42	7.78	7.88
Ash in dry . . . .	6.69	7.48	8.21	8.92
Nitrogen in dry . . . .	1.56	2.08	2.36	3.20
Dry organic matter consumed to produce 100 lbs. of live weight	lbs. 2288	lbs. 1321	lbs. 2371	The sheep lost weight

The turnips grown by superphosphate and alkalis only were over-ripe and pithy; the second lot, which gave the best result, were fully ripe; the third and fourth lots were not ripe. The most unripe and nitrogenous turnip gave, it is seen, the worst result when employed as food. For further information as to the effect of manures on the turnip-crop, see Mr. Lawes' paper (*Jour. Roy. Agri. Soc.* viii. 495).

Numerous experiments have been made upon the influence of manures on the percentage of sugar in beet-root. The manures which have the most favourable effect appear to be superphosphate and potash salts; as, however, such manuring yields a very small crop, a limited quantity of nitrogenous manure must also be applied. Any large application of nitrogenous manure so as to produce bulky roots will, except under exceptional conditions, greatly lower the proportion of sugar in the roots. In field experiments it is not unusual to find that the unmanured plot yields the roots richest in sugar.

The influence of the constituents of the soil on the composition of the ash of roots is considerable, as proved by the variations exhibited in different ash-analyses. Potash and soda are clearly replaceable to some extent. In the ash-analyses of which the mean has been already given (p. 1061), the variations were—in mangel-root: potash 69.2-25.2, soda 38.9-5.2; in sugar-beet: potash 58.9-22.0, soda 29.8-6.1; in carrots: potash 50.9-17.0, soda 34.8-10.1. From numerous experiments made on the continent, it appears that the supply of potash and phosphoric acid to sugar-beet is attended with a distinct rise of these substances in the ash. Manuring with chlorides has, however, the most marked effect. The percentage of chlorine may be readily doubled or tripled if a considerable amount of chlorides be applied in the manure. Common salt is frequently employed as a manure for mangels, and the amount of chlorides sometimes amounts to half the weight of the ash (49.5 p.c. Way). The analyses by Gilbert & Campbell of the ashes of the experimental turnips at Rothamsted point to the same general conclusions.

Assuming that average root-crops will be: turnips, 17 tons roots, root, & leaf

100 : 30; Swedes, 14 tons roots, root to leaf 100 : 15; mangels, 22 tons roots, root to leaf 100 : 37; sugar-beet, 10 tons roots, root to leaf 100 : 25; carrots, 10 tons roots, root to leaf 100 : 40\*; the quantities of the principal constituents removed in the crop will be in lbs. per acre about as follows. The total ash is reckoned without carbonic acid :—

	Nitro- gen	K <sup>2</sup> O	Na <sup>2</sup> O	CuO	MgO	P <sup>2</sup> O <sup>5</sup>	SO <sup>2</sup>	Cl	SiO <sup>2</sup>	Total ash
Turnips, root .	71	108.6	17.0	25.5	5.7	22.4	25.7	10.9	2.6	218
" leaf .	49	40.2	7.5	48.5	3.8	10.7	10.1	11.2	5.1	146
Total crop .	120	148.8	24.5	74.0	9.5	33.1	44.8	22.1	7.7	364
Swedes, root .	74	63.3	22.8	19.7	6.8	16.9	22.3	6.8	3.1	163
" leaf .	28	16.4	9.2	22.7	2.4	4.8	8.0	8.3	3.6	75
Total crop .	102	79.7	32.0	42.4	9.2	21.7	30.3	15.1	6.7	238
Mangel, root .	96	191.1	75.4	24.2	19.7	34.0	15.2	40.6	16.4	410
" leaf .	51	71.4	65.2	29.1	27.2	15.1	20.2	49.8	9.2	280
Total crop .	147	262.5	140.6	53.3	46.9	49.1	35.4	90.4	25.6	690
Sugar-beet, root .	53	76.8	16.6	10.2	15.2	23.0	7.5	3.0	6.1	160
" leaf .	21	25.6	19.4	22.8	21.2	8.5	9.2	6.7	3.6	117
Total crop .	74	102.4	36.0	33.0	36.4	31.5	16.7	10.6	9.7	277
Carrots, root .	35	72.2	40.4	21.3	10.1	21.8	13.5	9.6	3.9	195
" leaf .	50	44.0	45.5	80.2	9.7	9.5	20.5	22.2	13.0	250
Total crop .	85	116.2	85.9	101.5	19.8	31.3	34.0	31.8	16.9	445

The quantity of plant-food removed from the soil by root-crops is very large. An average crop of wheat, barley, or oats, will not contain more than 50 lbs. of nitrogen in corn and straw, nor more than 100 lbs. of ash-constituents, of which only about 30 lbs. will be potash and 19 lbs. phosphoric acid. Root-crops, if removed from the land, are therefore far more exhausting than corn-crops, and especially in respect of alkalis.

It was formerly imagined that the turnip, by means of its widespread foliage, was able to procure a large amount of nitrogen from the atmosphere, and that in this lay the secret of its usefulness in a rotation. The Rothamsted experiments have shown, on the contrary, that turnips are greatly dependent on the nitrogen of the soil, and, when they are grown for successive years with purely cinereal manures, impoverish the soil of nitrogen to a far greater extent than would result from a similar cropping of wheat or barley. It is probable, indeed, that a part of the advantage of turnip culture arises from the crop utilising soil-nitrogen existing in conditions unsuitable for cereal crops. Notwithstanding the greater capacity of root-crops for appropriating soil-nitrogen, nitrogenous manures must generally be employed if maximum crops are desired. Nitrates appear, from the experiments at Rothamsted, to have a distinctly greater effect both on Swedes and beet, than the same amount of nitrogen applied as ammoniac.

Turnips are apparently well able to supply themselves with alkalis from the soil, applications of potassium salts scarcely increasing the produce, except on poor light soils. The crop is, on the other hand, clearly deficient in the power of appropriating soil phosphates, applications of soluble phosphates producing a great effect on the crop. Turnips also appear more dependent on the soil for a supply of carbonic acid than is the case with cereal crops, organic manures, such as farmyard-manure and rape-cake, producing a relatively greater effect than with wheat or barley.

*Analysis of Roots.*—All adhering soil is first removed by washing, and the root wiped dry. Leaves and stalks are then cut off, and, in the case of sugar-beet analysed for manufacturing purposes, the green upper part of the root is also removed, as this is always separated by the sugar manufacturer. The root is then divided into quarters, or other convenient portions, by cutting it exactly through the middle from top to

\* The data for this proportion are very meagre.

bottom; thus prepared, each segment will fairly represent the whole, if the root is symmetrical. Water is determined in a segment of about 100 grms.; the weighed portion is cut into thin slices, strung on a wire, dried first at a very low temperature, and finally at  $110^{\circ}$ . Saccharine substances being difficult to desiccate, the drying is best completed in a current of dried air. The dry matter is very hygroscopic. Total nitrogen, ash, and fatty matter are determined in the powdered dry matter by the ordinary methods. To determine nitrogen present as nitrates, H. Schultze and E. Schulze (*Landw. Versuchs-Stationen*, ix. 445) extract 5–10 grms. of the powdered dry matter with hot 90 p.c. alcohol, evaporate the clear solution to dryness, dissolve in water, filter, and determine the nitric acid by Schlössing's method. For the determination of mark and cellulose, a segment of the root is reduced to pulp by rubbing on a grater; the pulp is then weighed, pressed in a cloth, the solid matter treated with water, again pressed, and the extraction with water continued as long as soluble matter is removed. In the case of turnips or beet the extraction of the pulp may be more conveniently performed on a vacuum filter, or by a method of Schulze described in the paper just referred to, but with roots containing starch the method given above is probably best. The insoluble matter, dried at  $110^{\circ}$ , gives the weight of crude fibre (mark), from which (in the case of turnip or beet) the percentage of sap in the root can be reckoned. The percentages of sap and mark are also often ascertained by Grouven's method, in which water is determined in a portion of filtered, undiluted sap, and also in the original root, and the calculation made according to the formula:  $x = \frac{a \times 100}{b}$ ,

in which  $a$  is the percentage of water in the root,  $b$  that in the sap, and  $x$  the percentage of sap in the root. This method is the only one that will yield the percentage of sap accurately in the case of roots containing starch. To determine cellulose, the crude fibre must be boiled with a dilute solution of soda to remove pectose, &c.; in roots containing no starch, boiling with dilute sulphuric acid may probably be omitted. See determination of fibre, *FODDER PLANTS* (p. 532). Sugar is determined in the watery extract of the pulp, or in the undiluted sap; if in the latter, the percentage of sap in the root must be ascertained by one of the methods already given. In the case of sugar-beet the best and speediest method of determining sugar is with the polariscope. A weighed quantity of the expressed sap is placed in a measured flask, treated with basic lead acetate, and water added to the mark, the whole well shaken and filtered. The tube of the polariscope is filled with the clear colourless filtrate, and an observation made. The reading furnished by the instrument expresses at once the percentage of cane-sugar in the sap. As the sap forms very uniformly 96 p.c. of ripe sugar-beet, this proportion is often assumed, and the percentage of sugar in the root calculated on this basis. The weight of sap to be taken, and the amount of its dilution, are fixed quantities, which depend on the kind of polariscope employed. For further information, see iii. 674, v. 471. In roots, as carrots, containing invert-sugar, Fehling's method may be employed. The sap is boiled and filtered, and the filtrate concentrated with some sulphuric acid to complete the inversion of the sugar. For further details see ii. 864. Starch may be approximately determined in carrots and parsnips by mixing the pulp with water, squeezing through a piece of fine linen, and repeating the operation till the water runs clear. The washings are then made alkaline with a little caustic soda, and allowed to stand. The deposited starch is collected, dried, and weighed.

R. W.

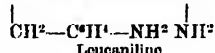
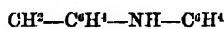
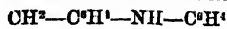
**ROSANILINE**,  $C^{20}H^{15}N^3$ . On the change of colour produced in rosaniline solutions by heat, see *LIGHT* (p. 747).

*Decomposition by Water* (Liebermann, *Deut. Chem. Ges. Ber.* v. 144; vi. 951).—Rosaniline and its salts are scarcely attacked by water at  $220^{\circ}$ ; but if the heating be continued for several hours at  $235^{\circ}$ , the tube after cooling is found to contain a wine-red liquid, considerable quantities of red needle-shaped crystals, ammonia (sal-ammoniac when the hydrochloride is operated on), a small quantity of resin, and phenol. The cold-filtered liquid gives off ammonia on evaporation, and deposits colourless crystals which gradually turn red. These crystals dissolve in boiling water and in alcohol, forming red solutions from which the compound separates in red needles having the composition  $C^{20}H^{15}NO^2.H^2O$ . This compound behaves like a weak acid, dissolves with cherry-red colour in ammonia, and is reprecipitated on neutralisation, but an excess of hydrochloric acid redissolves a large portion of the precipitate. Reducing agents convert it into a colourless substance. When the residue in the digestion-tube is washed with cold water and then exhausted with boiling water, the water on cooling deposits red needle-shaped crystals, part of which dissolves with red colour in ammonia, while the greater portion remains undissolved on the filter. The compound thus obtained may be recrystallised in the same way as the preceding, and gives, by analysis, numbers leading to the formula,  $C^{20}H^{15}N^3O.H^2O$ . It exhibits basic

properties; its solution in hydrochloric acid is precipitated by alkalis, and yields an oily compound with platinic chloride. It melts at 176°.

If the tubes are heated to 245°, the reaction appears to proceed in the same way; the resulting crystals, however, are not red, but yellow or colourless; and the crystals of both kinds thus obtained give by analysis the same numbers as the two corresponding kinds of red crystals, with the exception of a few tenths more per cent. of hydrogen. The yellow compounds are therefore the leuco-compounds of the red; the latter likewise exhibit partial reduction.

The following are regarded by Liebermann as the most appropriate constitutional formulae for rosaniline and leucaniline:



The reaction of rosaniline with water proceeds in a totally different manner when a little hydrochloric acid is added to the water. In this case at 240° the rosaniline salt is completely resolved into aniline and toluidine.

When rosaniline is heated with water in a copper digester to 270° a large quantity of phenol is formed, which may be got rid of by boiling the product with steam. The residuum contains carbonaceous matter and a compound containing no nitrogen, together with nitrogenous bodies. The latter are removed by boiling with water, and heating the crystals which separate out from the filtrate with crude hydrochloric acid, which dissolves only the nitrogen-compounds. The residuum crystallises from boiling water in pointed plates melting at 200°, and from alcohol in small plates. It dissolves in alkalis without colour, and with sodium-amalgam and water it gives a red solution, which soon becomes colourless. This compound contains C = 72.5; 72.6; 73.3; 73.4; and H = 5.0; 5.3; 5.8, or less than required for the formula  $\text{C}^{20}\text{H}^{14}\text{O}^2 + \text{H}^2\text{O}$ ; it does not change its composition at 170°. It has nothing in common with rosolic acid or with hydrosolic acid. By heating it with hydriodic acid to 160°, or with hydrochloric acid to 200°, it is resolved into phenol and cresol. Acetic anhydride converts it at 160° into a compound crystallising from alcohol in needles melting at 156°, and containing C = 68.25 and H = 5.21. Heated with phosphorus pentachloride containing trichloride to 170°, it yields the compound  $\text{C}^{20}\text{H}^{12}\text{Cl}^2\text{O}^2$ , crystallising from alcohol in colourless plates melting at 137°. This last compound is not changed by heating it with alcoholic potash, and gives up only part of its chlorine when boiled with sodium-amalgam.

**ROSE OIL.** See OILS VOLATILE (p. 872).

**ROSIN OIL.** On the preparation and purification of this oil, and its use as a lubricator for machinery, and in the preparation of railway and waggon grease, see *Dingl. pol. J.* cxi. 246; cxvii. 237; *Chem. Soc. J.* [2], xi. 304, 1175.

**ROSOCYANIN.** See CURCUMIN (p. 404).

**ROSOLIC ACID.** This name has been somewhat vaguely applied to a number of red compounds obtained from phenol by various reactions, but it is now restricted to the product, also called *pseudocoralin*, obtained by treating phenol with a mixture of oxalic and sulphuric acids (1st Suppl. 999, and p. 391 of this volume). Caro n. Wanklyn assign to it the formula  $\text{C}^{20}\text{H}^{10}\text{O}^4$ . H. Fresenius regards it as  $\text{C}^{20}\text{H}^{12}\text{O}^{10}$ .

Fresenius attributes the formation of rosolic acid on heating a mixture of oxalic acid and phenol with sulphuric acid, to the action of nascent carbon monoxide on sulphophenic acid; but, according to Prud'homme (*Bull. Soc. Chim.* [2], xix. 359), the presence of a conjugate phenol-acid is not essential, the sulphuric acid acting merely as a dehydrant. In fact, on replacing the sulphuric acid by boric, arsenious, or arsenic acid, or even on heating a mixture of phenol and dehydrated oxalic acid, rosolic acid is formed; moreover, the colouring matter is not produced on heating a mixture of crystallised oxalic acid and phenol. Prud'homme infers from these results that rosolic acid is a product of the direct action of nascent carbon monoxide on phenol, and that its constitution is correctly expressed by the formula  $\text{C}^6\text{H}^4.\text{COH.OH}$ , suggested by Kolbe (1st Suppl. 391).

Fresenius purifies rosolic acid by converting it into a magnesium salt; dissolving this salt in hot water, precipitating with sal-ammoniac, repeating this treatment till the aqueous solution of the magnesium salt is no longer coloured darker by an alkaline solution of potassium ferricyanide, and finally decomposing the magnesium salt with solution of hydrochloric acid, and crystallising the precipitate from alcohol or glacial acetic acid. The crystals are red by transmitted and green by reflected light, melt at 15.6° to a mass having the colour of cantharides, and give off water at a still higher temperature. By fusion with potash, rosolic acid is converted into a resinous mass, which is

resolved by sulphuric acid into a flocculent and a resinous mass, both of which are dissolved by ether and by alkalis. An alkaline solution of potassium ferricyanide added to the alkaline solution of the decomposition-products, gives rise to the reproduction of rosolic acid. Iron and acetic acid convert rosolic acid into leucorosolic acid. Strong nitric acid forms nitro-products, one of which is crystalline. When rosolic acid is distilled with potash, diphenyl appears to be formed, together with other products.

Rosolic acid is recommended by Schultze a. Märker (*Zeitschr. anal. Chem.* ix. 334) as an indicator in the estimation of carbonic acid by Pettenkofer's method (absorption of the carbonic acid by lime- or baryta-water of known strength, and subsequent titration with oxalic or hydrochloric acid). The rosolic acid is dissolved in alcohol and carefully neutralised with potash. A few drops of this tincture, added to the baryta- or lime-water, produce the deep red colour of barium or calcium rosolate, which is changed to a faint yellow by the slightest excess of acid. According to Schultze a. Märker this change of colour is more delicate than that afforded by litmus or turmeric.

Rosolic acid has been also recommended as an indicator in nitrogen determinations, when the evolved ammonia is absorbed by standard sulphuric acid; but in this case it does not give equally good results, since the colour which the liquid generally acquires from absorption of organic matter greatly interferes with the delicacy of its indications.

**ROTATING FURNACE** (Siemens'). See IRON METALLURGY (p. 702).

**RUBIDINE**,  $C^{111}H^N$ . This base has been detected in tobacco-smoke (see TOBACCO).

**RUBIDIUM**. This metal has been found in the ash of beet-root. To separate it, the mother-liquor left in preparing saltpetre from the ash of beet-root molasses is mixed with saw-dust and deflagrated, the charred mass exhausted with water, the solution evaporated to 1.317 sp. gr., and the sulphates and chlorides allowed to crystallise out. This second mother-liquor is mixed with hydrochloric acid, heated, filtered from precipitated sulphur, &c., and boiled with nitric acid till all iodine and bromine are expelled. The rubidium is now precipitated from the diluted solution by platinum tetrachloride, and separated in the usual way.

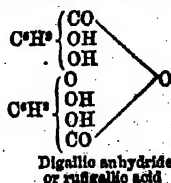
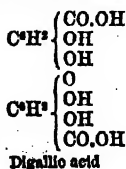
Direct experiment shows that one kilogram of the beet-ash of Northern France contains 1.75 grm. of rubidium chloride, and that the rubidium chloride is to the sodium chloride and potassium chloride as 1 to 126 and 331 (Pfeiffer, *Arch. Pharm.* [2], cl. 97; *Dingl. pol. J. cervi.* 498).

**RUE OIL**. The principal constituent of this oil is methyl-nonyl ketone,  $C^{11}H^{20} = CH^3.CO.C^9H^{19}$  (p. 808).

**RUFICARMIN.**  
**RUFICOCCIN.**

See COCHINEAL (pp. 367, 368).

**RUFIGALLIC ACID**,  $C^{11}H^8O^8$ .—This compound, which Robiquet obtained by heating gallic acid with sulphuric acid to  $140^\circ$ , is more easily produced by the action of sulphuric acid at  $80^\circ$ – $90^\circ$  on digallic acid,  $C^{14}H^{16}O^8$ , from which it differs by  $H^2O$ ; further, by the action of sulphuric acid on tetracetyl-tannic acid,  $C^{14}H^4(C^2H^3O)^4O^8$ ; similarly from ethyl gallate,  $C^8H^7(OH)^3.COOC^2H^5$ , with separation of alcohol, and from ethyl triacetyl-gallate,  $C^8H^4(C^2H^3O)^3.COOC^2H^5$ , with separation of ethyl acetate. Sulphuric acid acts therefore, in the formation of rufigallic acid, on the carbonyl groups, and as rufigallic acid no longer exhibits the properties of an acid, we may infer that it is nothing more than the anhydride of digallic acid:



Rufigallic acid can in fact take up four atoms of acetyl, forming the compound  $C^{14}H^4(C^2H^3O)^4O^8$ , which crystallises from boiling glacial acetic acid in small yellow or greenish-yellow prisms, sparingly soluble in alcohol even at the boiling heat. When treated with potash, these crystals turn yellow, and afterwards violet (H. Schiff, *Deut. Chem. Ges. Ber.* iv. 967), (see TANNIC ACID).

## S

**SABADILLA.** The alkaloids of sabadilla seeds have been examined by H. Weigelin (*Chem. Centr.* 1872, 220). The pounded seeds, freed from their capsules, are boiled with very dilute sulphuric acid, and the extract is treated with three times its volume of 80 p.c. alcohol to precipitate mucilaginous matters; after evaporation of the alcohol, the boiling solution is precipitated by ammonia, whereby a resinous mass is obtained containing veratrine, which may be purified by solution in ether, evaporation, solution of the residue in alcohol, and repeated precipitation by water. The ammoniacal filtrate is agitated with amyl alcohol, the extract evaporated, the residue dissolved in alcohol and precipitated with water, and the precipitate purified by animal charcoal: finally, the concentrated solution of the bases is precipitated by ammonia. Ether extracts from the precipitate a bright-red substance, subatrine,  $(C^{11}H^{10}N^2O)^+$ , and leaves behind sabadilline,  $C^{11}H^{10}N^2O^{12}$ , to be purified by solution in boiling water. The latter alkaloid is not absolutely insoluble in ether, and is not carbonised by sulphuric acid, but gives a yellow solution, becoming blood-red, and, finally, carmine-coloured; ammonia does not precipitate it from its salts, and alkaline carbonates give a turbidity only with boiling concentrated solutions (1 to 5). It is soluble in benzene, amyl alcohol, petroleum spirit, and chloroform, and crystallises from benzene, but not from water or alcohol; it does not produce sneezing or emetic action in frogs, but accelerates the action of the heart. Its gold salt,  $(C^{11}H^{10}N^2O^{12} \cdot 2HCl \cdot Au^2Cl^6)$ , is amorphous; its hydrochloride and sulphate are gummy.

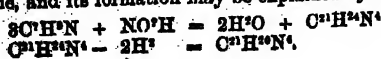
Subatrine much resembles sabadilline in properties; it gives two compounds with gold chloride, one amorphous =  $C^{11}H^{10}N^2O^7 \cdot 2HCl \cdot Au^2Cl^6$ , the other crystalline, =  $5(C^{11}H^{10}N^2O^7 \cdot 2HCl) \cdot 11Au^2Cl^6$ .

Veratrine can be obtained in two modifications, one of which is readily soluble in water. Weigelin finds the quantity of nitrogen contained in this alkaloid to be much less than that previously assigned to it, and represents it by the formula  $C^{12}H^{10}N^2O^{12}$  (compare v. 996).

**SACCHARIMETRY.** See SUGAR.

**SACCHARUMIC ACID,**  $C^{14}H^{12}O^{11} = C^{14}H^{12}O^8 \cdot 3H^2O$  (H. Reichardt, *Vierteljahrsschrift pr. Pharm.* xix. 384, 503). An acid formed, together with glucic acid (p. 556), by the action of baryta on grape-sugar. A mixture of baryta-water and grape-sugar deposits, when heated, a barium-compound, which is likewise obtained when the brown mass formed by melting grape-sugar with barium hydrate, is diluted with water as long as a precipitate forms. To obtain the acid contained in this precipitate free from glucic acid, the precipitate is suspended in water, and dilute sulphuric acid is added in quantity sufficient to produce a slight acid reaction. The filtrate mixed with lead acetate yields a precipitate of lead saccharumate; and by decomposing this precipitate with hydrogen sulphide, evaporating the filtrate at a gentle heat, and drying at  $80^\circ$ , saccharumic acid is obtained as a yellow-brown powder having an astringent taste, easily soluble in water and in alcohol, sparingly in ether. Its solution when exposed to the air gradually becomes darker, and deposits brown substances. Alkalis colour the acid solution darker. The acid decomposes the carbonates of calcium and barium, forming acid salts, like  $C^{14}H^{12}BaO^{11}$ . Lime-water produces a slight, baryta-water a more copious precipitate of the salt,  $C^{14}H^{12}Ba^2O^{11} + 5H^2O$ . Cupric salts give with neutral solutions a grey-brown precipitate having the composition  $C^{14}H^{12}Cu^2O^{11} + 3H^2O$ , which dissolves easily in free alkali and acid, and decomposes readily when heated. The precipitates thrown down from a neutral solution of the acid, by neutral and basic lead acetate, are respectively  $C^{14}H^{12}Pb^2O^{11}$  and  $C^{14}H^{12}PbO^{11}$ .

**SAFRANINE,**  $C^{11}H^8N^4$  (Hofmann a. Geyger, *Deut. Chem. Ges. Ber.* v. 526). A red dye prepared commercially, according to Mène (*Chem. News*, xxv. 215), by treating aniline with nitrous acid and arsenic acid successively, the higher-boiling portions of aniline oil being best adapted for the purpose. Hofmann a. Geyger find that this process yields but a small quantity of safranine, mixed with a large amount of secondary products, and that the preparation of safranine succeeds best when chromic acid is used as the oxidising agent instead of arsenic acid. Safranine cannot, however, be prepared from pure aniline or solid toluidine, or a mixture of the two, but it can be obtained from liquid toluidine boiling at  $198^\circ$ . Safranine appears therefore to be a derivative of toluidine, and its formation may be explained by the equations:



Safranine is met with in commerce in the form of a paste, and of a yellowish-red powder, which contains the hydrochloride of the base mixed with calcium carbonate and common salt. On boiling this with water, and allowing the solution to cool, a crystalline substance separates, which, after repeated recrystallisation from water, will be found to leave no residue when burnt. It, however, loses hydrochloric acid by these operations, and becomes more soluble, so that the addition of hydrochloric acid to the mother-liquors causes a further separation of the crystalline hydrochloride.

The free base is obtained by decomposing the solution of the hydrochloride with silver oxide, and evaporating the deep red liquid. On cooling, red-brown crystals are deposited, which closely resemble the hydrochloride in appearance. Safranine dissolves easily in water and in alcohol. Dried at  $100^{\circ}$ , it acquires a faint greenish metallic lustre. The addition of hydrochloric acid to the aqueous solution of the base precipitates safranine hydrochloride.

The most characteristic reaction of safranine is that when strong hydrochloric acid, or, better, sulphuric acid, is gradually added to its solutions, the colour changes first to a fine violet, and then successively to blue, dark green, and light green. On diluting the solution, the same changes of colour are observed in reverse order.

*Safranine Hydrochloride*,  $C^{21}H^{20}N^4.HCl$ .—To obtain the normal hydrochloride, it is necessary to acidify the boiling solution of the salt with hydrochloric acid. It forms thin reddish crystals, which are soluble in water and in alcohol, especially when heated. It is insoluble in ether and in a concentrated solution of salt. Both the aqueous and alcoholic solutions have an intensely yellowish-red tint. The addition of ether to the latter solution causes the precipitation of the hydrochloride.

The *platinochloride*,  $2(C^{21}H^{20}N^4.HCl).PtCl_4$ , is obtained by precipitating a warm solution of the hydrochloride with excess of platinum chloride, and washing the precipitate with dilute hydrochloric acid. It is a crystalline yellowish-red powder, almost insoluble in water, alcohol, and ether.

*Safranine Hydrobromide* is precipitated in microscopic needles on adding hydrobromic acid to a solution of the base. It is almost insoluble in cold, but soluble in boiling water. The addition of bromine to a solution of the hydrochloride causes a precipitate which, when recrystallised from water, yields needles having a metallic green lustre. The *hydriodide* is similar to the hydrobromide.

*Safranine Nitrate*,  $C^{21}H^{20}N^4.HNO_3$ .—On adding an excess of dilute nitric acid to a hot aqueous solution of the free base, and leaving the liquid to cool, the nitrate separates in fine red-brown needles, which are difficultly soluble in cold, but readily in hot water. It is decidedly less soluble than the hydrochloride.

*Safranine Sulphate* is a moderately soluble salt, precipitated by the addition of sulphuric acid to a concentrated solution of the base. On warming the liquid it redissolves, and separates again in fine needles on cooling. The *oxalate* is very similar, but somewhat less soluble. The *acetate* is very soluble.

*Safranine Picrate*,  $C^{21}H^{20}N^4.C^8H^4(NO_2)_3O$ .—When picric acid is added to a dilute solution of safranine hydrochloride or nitrate, the picrate is precipitated in brownish-red needles which are insoluble in water, alcohol, or ether.

**SAHLITE.** *Calcio-magnésio-ferruginous Augite*.—This mineral occurs, together with graphite, in some of the dense limestones imbedded in the mica- and hornblende-slate of Valpellina in the Pennine Alps. The augite forms rounded grains having a fused appearance, generally from  $\frac{1}{2}$  to 1 mm. in size, and of a bluish colour on the outside, whitish-grey within. Some of these grains exhibit crystalline faces, namely, those of the vertical prism of augite, and of the ortho- and clinopinacoid. They exhibit distinct cleavage in two directions parallel to the faces of the vertical prism, indistinct, parallel to the clinopinacoid. Before the blowpipe the mineral melts easily and with violent intumescence. Sp. gr. = 3.320. Loss by ignition 0.14 p.c. Analysis gave:

SiO <sup>2</sup>	CaO	MgO	FeO	AlPO <sup>4</sup>	
54.02	24.88	13.62	8.07	0.20	= 100.60,

which, neglecting the alumina, agrees nearly with the formula  $(\frac{1}{2}FeO.\frac{1}{2}MgO.\frac{1}{2}CaO)SiO_2$  or  $FeMg^2Ca^4Si^6O^{24}$  (calc. 53.57 SiO<sup>2</sup>, 25.00 CaO, 13.39 MgO, 8.04 FeO).

**SALANT.** This name is applied, in the Departments bordering on the Mediterranean, to a thin saline incrustation, which in some places completely covers barren lands, and in others forms isolated barren spots in the fertile soil. These spots consist essentially of sodium chloride mixed with 6 to 10 p.c. calcium sulphate. The analysis of the soils on which they occur gave in 100 pts.—(1) on the surface; (2) 30 c.m. deep; (3) from a salant spot in the midst of a cultivated soil, which close to it con-



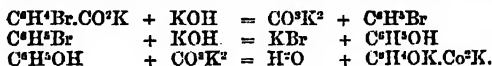
tained only 0.0002 of the salts. The samples examined were from Agde, in the Department of Hérault:

	NaCl	CaSO <sup>4</sup>	MgSO <sup>4</sup>
(1)	6.163	0.176	0.228
(2)	0.761	0.051	0.129
(3)	0.845	—	0.300

(E. P. Bérard, *Compt. rend.* lxxiii. 1155).

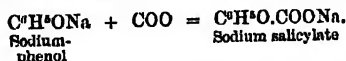
**SALICYLIC ACID**,  $C^6H^4O^2 = C^6H^3OH.CO^2H$ . *Formation and Constitution.*—On the formation of salicylic acid from sulphobenzoic acid, and from orthotoluene-sulphonic acid, and the proofs that it belongs to the ortho- (1 : 2) series, see pp. 134, 135.

Hübner (*Ann. Chem. Pharm.* clxii. 71) finds that when ordinary bromobenzoic acid (purified by several crystallisations and melting at 155°) is fused with potassium hydrate, salicylic acid is formed as well as oxybenzoic acid; whereas the latter, which is the analogue of ordinary bromobenzoic acid, might be expected to be the sole product. As, however, salicylic acid is known to be formed by the action of potassium carbonate on phenol, its production in this case may be supposed to take place in the manner represented by the following equations, the bromobenzoic acid being first converted into bromobenzene, then into phenol, and the phenol into salicylic acid:

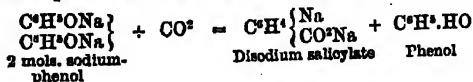


*Preparation.*—The preparation of salicylic acid from wintergreen oil being very expensive when large quantities are required, Kolbe (*J. pr. Chem.* [2], x. 89) has endeavoured to improve the method of obtaining it from phenol, devised by himself and Lautemann some years ago (v. 153).

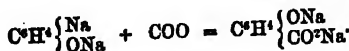
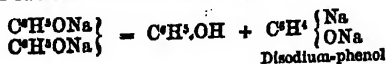
Sodium-phenol is prepared by dissolving crystallised phenol in a strong solution of commercial soda (in the exact proportions of the molecular weights, as an excess of phenol causes the product to be highly coloured, and diminishes the yield of salicylic acid), evaporating to dryness in iron vessels, and finally heating the pasty mass over a flame, stirring all the while. The sodium-phenol, being very hygroscopic, should be placed when hot in stoppered bottles, as moisture diminishes the yield of acid. The sodium-phenol is then heated in a retort to 100°, a slow stream of carbonic anhydride is passed through the apparatus, and the temperature after many hours is allowed to rise to 180°. Phenol then distils over, till the temperature rises to 220°–250°, the operation being completed when no more phenol passes over at this temperature. It was supposed that the reaction would take place as follows:—



but as the retort contained basic sodium salicylate, and phenol distilled over, the process evidently takes place according to the following formulæ:



which is the result of two simultaneous reactions:



On decomposing the basic salt with hydrochloric acid, the salicylic acid is separated, and can be purified by dissolving it in etherated alcohol, boiling with soda, and again decomposing by acid.

Salicylic acid is also formed, but in smaller quantities, when barium or calcium phenol is used. Potassium-phenol gave various results, at one time salicylic acid, at another time paraoxybenzoic acid. Those irregularities were at first considered to be due to the presence of sodium in the potassium used, but they are now attributed to the influence of the heat at which the operation is performed. To determine this two series of experiments were instituted. Potassium-phenol, prepared in the same manner as the sodium-phenol, when heated for four hours at 100°, and subjected to the action of carbonic anhydride, yielded but a small amount of acid, consisting wholly

of salicylic acid. When it was heated to 135°, and carbonic anhydride then passed through it, the temperature being allowed to rise to 145°, phenol was produced, and a large amount of salicylic acid, but no paraoxybenzoic acid. But when carbonic anhydride was allowed to act first at 170°, and the temperature then raised to 200°–210°, phenol distilled in its proper proportions, and a large amount of paraoxybenzoic acid was formed without a trace of salicylic acid.

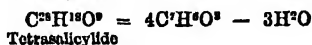
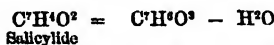
In other experiments carbonic anhydride was passed through heated phenol, and when the temperature had risen to 130°, potassium was added till it rose to 150°. When the equivalent quantity of potassium had been added, the product yielded pure salicylic acid. Another portion of phenol saturated with potassium yielded a distillate of phenol at about 200°, and the retort contained a considerable quantity of paraoxybenzoic acid free from salicylic acid. If sodium-phenol be treated with carbonic anhydride at 240°–280° for four hours, pure salicylic acid is produced without a trace of paraoxybenzoic acid.

From a mixture of salicylic and paraoxybenzoic acids, the greater part of the salicylic acid may be separated in the form of a sparingly soluble basic calcium salt, by mixing the aqueous solution of the acids with excess of milk of lime. A more exact method of separation, however, is to dry the mixture of acids at 100° and digest it in boiling chloroform, which dissolves the salicylic acid easily, and takes up but little of the paraoxybenzoic acid (Kolbe).

On the Heat of Combination of Salicylic acid with Bases, see HEAT (p. 62).

**Physiological action.**—Given in large doses (6 grams in two days) salicylic acid produces singing in the ears, and passes out in the urine, partly as salicylic acid, partly unchanged; it may also be detected in 2 hours, and even after 20 hours in urine, although the dose may be only 0.3 gram. Owing to the fact that it is easily decomposed into phenol and carbonic anhydride, it acts antiseptically, preventing fermentation and decomposition, and may therefore be applied to the preservation of meat. For this latter purpose it is preferable to phenol, as it is tasteless, or nearly so. Neither paraoxybenzoic nor oxybenzoic acid acts antiseptically. Salicylic acid has also been applied to the dressing of wounds, and has been found to work very satisfactorily, aiding granulation, &c., and preventing fever (Kolbe, *loc. cit.*)

**Action of Phosphorus oxychloride.**—With this reagent, salicylic acid yields condensation-products. The portion of the product insoluble in hot water contains the compounds:



The former crystallises from boiling alcohol, the latter is a solid brittle resin.

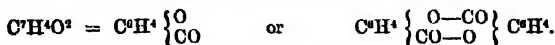
**Nitrosalicylic acid** is likewise attacked by phosphorus oxychloride (H. Schiff, *Deut. Chem. Ges. Ber.* iv. 969).

**Iodosalicylic Acid.** Hlasiwetz and Weselsky (*ibid.* v. 380) have succeeded in replacing part of the hydrogen in salicylic acid and its isomerides by iodine, by the process which they formerly applied to the formation of iodophenols (*1st Suppl.* 910), viz. the action of iodine in presence of mercuric oxide. Salicylic, oxybenzoic, and paraoxybenzoic acid when thus treated exhibit different degrees of capability of taking up iodine in exchange for hydrogen.

**Nitrosalicylic Acids.** When salicylic acid is nitrated, not only is ordinary nitrosalicylic acid formed, but also two more soluble isomerides, one of which crystallises in long colourless needles melting at 124°. This modification dissolves sparingly in cold water, readily in hot water and alcohol, and gives, with ferric chloride, a reddish-blue colour. The *potassium salt*,  $\text{C}^6\text{H}^4(\text{NO}^2)\text{OK.CO}^2\text{K}$ , crystallises from hot water in long yellow needles. The *magnesium salt*,  $\text{C}^6\text{H}^4(\text{NO}^2)\text{O.CO}^2\text{Mg} + 3\text{H}^2\text{O}$ , forms yellow needles which readily dissolve in hot water. The *barium salt*,  $(\text{C}^6\text{H}^4(\text{NO}^2)\text{OH.CO}^2)^2\text{Ba}$ , crystallises from a hot aqueous solution in scales, and from a dilute in slender needles. The *lead salt*,  $\text{C}^6\text{H}^4(\text{NO}^2)\text{O.CO}^2\text{Pb}$ , is a yellow precipitate. The *silver salt*,  $\text{C}^6\text{H}^4\text{NO}^2\text{OH.CO}^2\text{Ag}$ , is readily soluble and forms glistening brownish needles. The second isomeric acid remains in the mother-liquor of the barium salt of the first, and crystallises in long colourless needles melting at 218°. Its *barium salt*,  $(\text{C}^6\text{H}^4(\text{NO}^2)\text{OH.CO}^2)^2\text{Ba} + 4\text{H}^2\text{O}$ , forms hard, light yellow, compact crusts (L. B. Hall, *Deut. Chem. Ges. Ber.* vii. 1820).

**SALICYLIC ALDEHYDE, or SALICYLOL, C}^6\text{H}^4\text{O}^1**. This compound, treated with phosphorus oxychloride, yields a purple-red, non-crystallising product which dissolves in alkalis with splendid violet colour (Schiff).

**SALICYLIC ANHYDRIDES.** Several anhydrides of salicylic acid have been described by Gerhardt (v. 160) and by Kraut (1st Suppl. 1007). Schiff (*Ann. Ch. Pharm.* clxiii. 218) prepares salicylide,  $C^6H^4O^2$ , and tetrasalicylide,  $C^{24}H^{16}O^8$ , by the action of phosphorous oxychloride on salicylic acid. This acid when heated dissolves easily in the oxychloride, with abundant evolution of hydrochloric acid. At the end of the reaction the liquid is decanted from the separated metaphosphoric acid, the excess of oxychloride is distilled off, and the residue is decomposed, while well cooled by throwing in lumps of ice. The mass, which soon solidifies, is boiled with water to remove unaltered salicylic acid, and treated several times with boiling alcohol. The alcoholic solution yields, by repeated crystallisation, large spherical groups of shining needles which shrink up very much when dried. These crystals consist of salicylide:



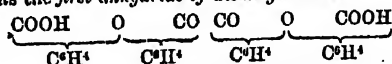
The reaction takes place in the manner represented by the equation:



Salicylide is insoluble in water, does not give the purple reaction with iron salts, or a precipitate with lead salts, and is not attacked by acetyl chloride. It melts for the most part at  $195^{\circ}$ - $200^{\circ}$ , but decomposes partially at the same time, so that the whole does not become liquid till heated to  $220^{\circ}$ - $225^{\circ}$ . By boiling with potash it is reconverted into salicylic acid.

The portion of the original product which is nearly insoluble in boiling alcohol, forms a white hard resinous mass, insoluble in water, and only slightly soluble in alcohol, ether, and benzine, even at the boiling heat. The results of its analysis agree very well with the formula  $C^{24}H^{16}O^8 = 4C^6H^4O^2 - 3H^2O$ , which is that of Kraut's tetrasalicylic acid; Schiff calls it tetrasalicylide. It softens at  $205^{\circ}$ , is perfectly fluid at  $230^{\circ}$ , and decomposes at about  $250^{\circ}$ . Strong sulphuric acid dissolves it with yellow colour, and water partly precipitates it from the solution unaltered, partly converts it into salicylic acid. When heated with strong sulphuric acid it forms sulphosalicylic acid.

As tetrasalicylide exhibits no iron reaction, and does not yield any acetyl derivative, it may be regarded as the first anhydride of disalicylic acid:



To Gerhardt's salicylic anhydride, which Kraut designates as *Salicylo-salicylic acid*,

Schiff assigns the formula,  $C^6H^4 \left\{ \begin{array}{c} \text{COOH} \\ O \\ \text{COOH} \end{array} \right\} C^6H^4$ , as otherwise its formation from aceto-

salicylic acid should be attended with the elimination of an atom of acetyl in the form of acetic acid, and the presence of a phenolic hydroxyl should give rise to the well-known iron reaction, which is not the case.

The existence of Kraut's *trisalicylo-salicylic acid* is doubted by Schiff, inasmuch as the more exact calculation of the analyses given by Kraut does not yield very accordant results. Kraut, on the other hand (*Ann. Ch. Pharm.* clxv. 159), upholds the existence of the acid in question, and the correctness of the analytical numbers which he obtained.

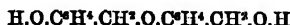
**SALIGENIN and SALIRETIN.** Kraut (*Ann. Ch. Pharm.* cl. 123) prepares saliretin by drenching finely-pulverised salicin with 10 pts. fuming hydrochloric acid of sp. gr. 1.125, warming the solution with agitation, and then heating it to  $80^{\circ}$ , whereupon part of the saliretin produced separates as a pulverulent precipitate. The precipitation is completed by pouring the pasty mass into a large quantity of water; the precipitate is washed till free from chlorine, and dissolved in moderately dilute spirit, a small quantity of gelatinous matter then remaining undissolved; and the saliretin is separated by pouring the filtrate into a large quantity of salt water. It then falls down quickly in curdy flocks, whereas pure water merely renders the alcoholic solution turbid.

Saliretin thus prepared is a yellowish or reddish-yellow powder. After drying over oil of vitriol, it gives off no more water at  $100^{\circ}$  or even at  $200^{\circ}$ , but cakes together and turns brown at the latter temperature. It is soluble in aqueous alcohol, and if its preparation has been conducted at the temperature above mentioned, it likewise dissolves almost completely in absolute alcohol. If, on the other hand, salicin has been decomposed by hydrochloric acid at a temperature not exceeding  $40^{\circ}$ , the solution of the product in aqueous alcohol yields, on addition of absolute alcohol, a precipitate, which however does not differ from saliretin either in composition or in properties.

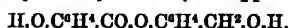
Saliretin is commonly represented by the formula  $C^7H^6O$  or  $C^{14}H^{10}O^2$ ; but Kraut's analysis leads to the formula  $C^{14}H^{10}O^2$ , originally suggested by Moitessier (*Jahresb. f. Chem.* 1866, 677), who regarded saliretin as related to saligenin, in the manner as an ether to a monatomic alcohol:



Kraut, however, regards saliretin, not as the ether of saligenin, but as *saligeno-saligenin*:



a compound analogous to salicylo-salicylic acid (1st Suppl. 1007):



Saliretin is likewise precipitated by salt water from its alkaline solution, and the precipitate, after continuous washing with the same liquid, contains, after deduction of sodium chloride, a quantity of soda less than sufficient to form a saturated or half-saturated sodium-compound.

Piria found that saliretin, when oxidised by chromic acid, does not yield salicylol; and Kraut finds that, when oxidised by potassium permanganate, it does not yield either salicylol or salicylic acid, or in general any well-characterised product of decomposition.

A substance called saliretin, which Gerhardt prepared by the action of sulphuric acid on saligenin, exhibits the composition of trisaligeno-saligenin,  $C^{24}H^{18}O^6 = 4C^7H^6O^2 - 3H^2O$ ; some resinous products prepared by Beilstein & Seelheim (*Jahresb.* 1861, 765) from saligenin, by the action of acetic anhydride or ethyl iodide, appear to consist of *heptasaligeno-saligenin*,  $C^{56}H^{42}O^8 = 8C^7H^6O^2 - 7H^2O$  (Kraut).

*Action of the Acetyl-derivatives of Sugars on Sodium-saligenin.*—Acetyl-glucose and sodium-saligenin, heated together in presence of alcohol or benzene, yield a small quantity of a substance which forms glucose and saliretin when boiled with dilute sulphuric acid. This substance is obtained pure by evaporation to dryness, solution in water, precipitation by lead acetate, and decomposition by hydrogen sulphide; and, finally, by evaporation to dryness in a vacuum, there is obtained an amorphous, yellowish, brittle mass, soluble in water and in alcohol. The greater part of the substances employed, however, react differently, producing acetosaliretin and sodium glucinate; the former of these, which, by saponification, yields saliretin and sodium acetate, is likewise formed by the action of acetic anhydride on saliretin (Schützenberger, *Ann. Chim. Phys.* [4], xxi. 235).

Diacetosaccharose and sodium-saligenin, heated in an open vessel with absolute alcohol, also form a small quantity of a glucoside which splits up into glucose and saliretin; the greater portion of the substance, however, is converted into acetosaliretin, and the sodium salt of an acid very similar to glucinic acid, which may be termed *saccharinic acid*. This sodium salt,  $C^{12}H^{10}NaO^4$ , separates from boiling absolute alcohol in small, white crystals; it is very soluble in water, gives with basic lead acetate a precipitate soluble in excess of the acid, and yielding the acid itself by decomposition with hydrogen sulphide; the acid forms a very sour syrup (Schützenberger).

The lead precipitate obtained by treating saligenin with lead acetate also yields, when heated with an aqueous solution of acetyl-glucose or acetyl-saccharose, a considerable quantity of a glucoside, which, when treated with acids, splits up into saliretin and glucose (Schützenberger).

**SALINE SOLUTIONS.** On the Capillarity of Saline Solutions, and its relation to their Density, see pp. 243, 244.

On the Electrolysis of Saline Solutions, see ELECTRICITY (pp. 460-462).

On the Specific Heat of Saline Solutions, see HEAT (pp. 596-601).

*Solidifying Points of Saline Solutions.*—L. G. de Coppet (*Ann. Chim. Phys.* [4], xxii. 366-406; xxv. 502-553; xxvi. 98-121) has made elaborate experiments on the lowering of the freezing point and point of maximum density of saline solutions below those of pure water, and has applied the results to the determination of the chemical constitution of the solutions. The experiments of Rüchhoff on the freezing of water from saline solutions (iii. 80; also *Pogg. Ann.* cxiv. 63; cxvi. 55; *Jahresb. f. Chem.* 1861, 56; 1862, 23) have shown that if  $M$  denotes the amount of anhydrous salt in 100 pts. of water, and  $E$  the lowering of the freezing point of the solution below  $0^\circ$ , the ratio  $\frac{E}{M}$  is sometimes constant, sometimes increases with the increase of

$M$ ; and, assuming that, in the former case, the salts are present in the solutions in the anhydrous state, and in the second, in combination with a certain number of molecules,  $r$ , of water of hydration, it follows that if  $M_r$  denotes the amount of this hydrate in 100 pts. of water, the ratio  $\frac{E}{M_r}$  is constant. De Coppet recognises a third case, in

which  $\frac{E}{M}$  decreases with increase of  $M$ , and he further finds that in many cases in

which  $\frac{E}{M}$  increases, no value of  $r$  can be found for which the ratio  $\frac{E}{M_r}$  is constant.

To explain these two cases, De Coppet supposes that, in the solutions in question, a partial decomposition (dissociation) of the salt takes place, in such a manner that in many cases the dissociation extends only to the state of hydration of the salt, while in others the salt itself is modified by the action of the water, so that the solution contains a mixture of compounds, the proportion between which varies with the concentration and the temperature. This decomposition of a hydrate dissolved in water may be compared with that of a hydrated salt in a limited space filled with aqueous vapour (1st Suppl. 425), the quantity of water combined with a dissolved salt depending, not only on the temperature, but likewise on the degree of concentration of the solution.

Denoting by  $E$  and  $D$  the depressions of the freezing point and of the maximum density of a solution, and by  $M$  the amount of anhydrous salt in 100 pts. of water, De Coppet draws from the whole of his investigation the following conclusions:

1. If the ratios  $\frac{E}{M}$  and  $\frac{D}{M}$  are both constant between given limits of pressure and temperature, it may be inferred that between these limits the salt is present in the solution in the anhydrous state.
2. If the ratios  $\frac{E}{M}$  and  $\frac{D}{M}$  increase as  $M$  increases, the solution will contain at least one compound formed at the expense of the solvent. If solutions, between certain limits of temperature and concentration, contain only one hydrate, the number of water molecules  $r$  in the latter may be calculated by the following formula established by Müldorff (Pogg. Ann. cxvi. 62):

$$r = \frac{100A(M't - M't')}{18MM'(t - t')}$$

in which  $A$  is the molecular weight of the salt  $M$ , and  $M'$  two different quantities of the dissolved salt,  $t$  and  $t'$  the corresponding freezing points.

3. If the ratios  $\frac{E}{M}$  and  $\frac{D}{M}$  decrease as  $M$  increases, the salt in the solution has probably been altered by the action of the solvent.

These conclusions, taken in their strict sense, are applicable to each particular solution only at its freezing temperature or at the point of maximum density.

The following table (p. 1070) exhibits some of the numerical results of De Coppet's experiments. The second column contains the formulae of the anhydrous salts or hydrates which are supposed to exist in the solution at the freezing point; those hydrates which are not yet known in the solid state are distinguished by an asterisk. The fourth and fifth columns exhibit the coefficients of depression of the freezing point  $h$ , referred to the unit of weight of substance dissolved in 100 pts. of water, and the depressions of the freezing point  $H$ , referred to one molecule.

From this table it appears that bodies belonging to the same molecular group exhibit nearly equal molecular depressions of the freezing point. Potash and soda are related to the group including the chlorides, bromides, and iodides of the alkali-metals; but for the group including the chlorides, bromides, and iodides of the alkali-metals and alkaline ammonia the molecular depression is not much more than half as great, whence De Coppet infers that the constitution of ammoniacal solutions differs from that of solutions of potash and soda.

A similar relation exists between the molecular weights of salts and the lowering of their temperatures of maximum density, and affords, for a large number of salts, in default of direct observations, the means of calculating the temperatures of freezing, and of the maximum density of their aqueous solutions. De Coppet, indeed, by comparing the two kinds of molecular depression, arrives at the general conclusion that for each group of the chlorides, bromides, and iodides of the alkali-metals and alkaline earth-metals, for caustic potash and soda, and probably for a large number of other bodies of corresponding chemical constitution, the molecular depression of the temperature of maximum density of aqueous solutions is nearly four times as great as the molecular freezing point depression. For that particular solution of each substance for which the freezing point coincides with the point of maximum density, both these temperatures are situated, within a few hundredths of a degree, at  $-1.33^\circ$ .

*Depression of the Freezing Points of Saline Solutions.*

		Molecular weight $\Lambda$	Coefficient of depression $\Lambda$	Depression for 1 molecule $\Pi = \Lambda \cdot A$
Potassium chloride . .	KCl	74.6	0.451	33.6
" bromide . .	KBr	119.1	0.292	34.8
" iodide . .	KI	166.0	0.212	35.2
Sodium chloride . .	NaCl.2H <sup>2</sup> O	94.5	—	33.8
" " " " {	NaCl.3H <sup>2</sup> O	112.5	—	31.4
" bromide . .	NaBr.3H <sup>2</sup> O*	157.0	0.216	33.9
" iodide . .	NaI.3H <sup>2</sup> O*	203.9	0.170	34.7
Ammonium chloride . .	NH <sup>4</sup> Cl	53.5	0.650	34.8
Potassium hydrate . .	KHO.2H <sup>2</sup> O	92	—	33.9
Sodium " . .	NaHO.1.5H <sup>2</sup> O	67	—	34.1
Ammonia . .	(NH <sup>3</sup> )HO*	35	0.542	19.0
Barium chloride . .	BaCl <sup>2</sup> .15H <sup>2</sup> O*	478.2	—	43.1
Strontium " . .	SrCl <sup>2</sup> .16H <sup>2</sup> O*	428.5	—	41.6
Calcium " . .	CaCl <sup>2</sup> .16H <sup>2</sup> O*	381	0.1135	43.2
Cupric " . .	CuCl <sup>2</sup> .12H <sup>2</sup> O*	350.5	0.127	44.5
Manganous " . .	MnCl <sup>2</sup> .12H <sup>2</sup> O*	342.2	0.138	47.2
Potassium nitrate . .	KNO <sup>3</sup>	101	0.267	27.0
Sodium " . .	NaNO <sup>3</sup>	85	0.310	26.4
Potassium carbonate . .	K <sup>2</sup> CO <sup>3</sup> .6H <sup>2</sup> O*	246	0.161	39.6
" chromate . .	K <sup>2</sup> CrO <sup>4</sup>	194.5	0.196	38.1
" sulphate . .	K <sup>2</sup> SO <sup>4</sup>	174	0.201—0.224	35.0—39.0
Ammonium " . .	(NH <sup>4</sup> ) <sup>2</sup> SO <sup>4</sup>	132	0.276	36.4
Ferrous sulphate . .	FeSO <sup>4</sup> .7H <sup>2</sup> O*	278	0.055	15.3
Zinc " . .	ZnSO <sup>4</sup> .7H <sup>2</sup> O	287	0.055	15.8
Magnesium " . .	MgSO <sup>4</sup> .7H <sup>2</sup> O	246	0.073	18.0
Cupric " . .	CuSO <sup>4</sup> .5H <sup>2</sup> O	249.5	0.070	17.5

The numbers in the following table afford examples of the above-mentioned decrease of the ratio  $\frac{\Pi}{M}$  with increase of  $M$ . Those distinguished by an asterisk refer to supersaturated solutions.

*Depression of the Freezing Point of Solutions of:*

Sodium Sulphate			Sodium Nitrate			Ammonium Nitrate		
M	$\Pi$	$\frac{\Pi}{M}$	M	$\Pi$	$\frac{\Pi}{M}$	M	$\Pi$	$\frac{\Pi}{M}$
2	0.6°	0.300°	12	4.25°	0.354°	2°	0.83°	0.415°
2.03	0.6	0.295	20	6.7	0.335	5	2.03	0.406
4	1.2	0.300	—	6.7	0.335	6	2.4	0.400
4.06	1.2	0.295	30	9.7	0.323	10	3.85	0.385
5*	1.4	0.280	40	12.7	0.318	12	4.55	0.379
5.08*	1.45	0.285	50	15.7	0.314	20	6.9	0.345
6.09*	1.7	0.286	—	15.4	0.308	30	9.35	0.313
10	2.75	0.275	—	15.4	0.308	—	9.35	0.312
10.15*	2.7	0.266	60	18.8	0.313	40	11.75	0.294
12.2*	3.05	0.250	—	18.6	0.310	50	13.6	0.272
15*	3.65	0.243	70	21.55	0.308	60	15.6	0.260
15.2*	3.65	0.240	—	21.8	0.311	70.24	17.4	0.245
20	4.05	0.225	—	—	—	—	—	—

For De Coppet's experiments on the depression of the freezing point in *solutions of mixed salts*, and for his comparison of his own results with the conclusions arrived at by Wüllner in his Memoir on the Tension of the Aqueous Vapour from Saline Solutions (iii. 95), see the original paper (*Ann. Chim. Phys.* [4], xxvi. 98).

From experiments by Rüdorff (*Pogg. Ann.* cxlv. 599), it appears that the molecular decrease of the ratio  $\frac{E}{M}$  with increase of  $M$  is most strikingly exhibited in solutions of *silver nitrate*, in which it varies from  $0.175^\circ$  to  $0.108^\circ$  between  $M = 4$  and  $M = 62$ , and of *acetic acid*, in which it decreases from  $0.325^\circ$  to  $0.237^\circ$  between  $M = 2$  and  $M = 62$ .

*Contraction accompanying the Solution of Salts.*—The following observations on this phenomenon have been made by Valson (*Compt. rend.* lxxiii. 1376). For very soluble salts the contraction continually diminishes down to an imperceptible amount, as the contraction approaches its maximum.

With regard to strength of contraction, the substances examined form the following series:—1. According to the *metalloidal radicles*: Carbonates, sulphates, chlorides, nitrates, iodides. 2. According to the *metallic radicle*: Iron, zinc, copper, magnesium, strontium, barium, calcium, sodium, lead, potassium, ammonium. Hydrated salts exhibit a much smaller coefficient of contraction than the corresponding anhydrous salts, and the contraction is smaller the greater the number of molecules of water of crystallisation. Hence the chief part of the contraction appears to be completed in the formation of the crystal itself with the first molecule of crystallisation-water which the anhydrous salt takes up. Amongst anhydrous salts, those which crystallise appear to have the smallest coefficients of contraction. On the other hand, the number of molecules of crystallisation-water is greater as the coefficient of contraction referred to the anhydrous salt is higher. (See also pp. 293–304.)

*Solubility and Density of Solutions of Potassium and Sodium Salts.*—Page a. Keightley (*Chem. Soc. J.* [2], x. 566) have determined the density and saline contents of saturated solutions of the chloride, nitrate, and sulphate of potassium and of the nitrate and chloride of sodium at  $15.6^\circ$ ; also the density of each of these salts in the solid state at  $15.6^\circ$ , and the solubility of each in presence of one or two of the others. The solutions were prepared at the constant temperature of  $15.6^\circ$ . When two numbers are attached in the following table to the same salt, the second refers to a solution saturated at  $100^\circ$  and cooled to  $15.6^\circ$ .

*Solubility and Specific Gravity at  $15.6^\circ$ .*

Salt	Amount of Salt		Amount of water to 1 pt. of salt	Specific gravity	
	In 100 pts. of saturated solution	to 100 pts. of water		of the saturated solution	of the salt
NaCl	26.24	35.76	2.79	1204.03	2.08
	26.61	36.26	2.75	1206.93	
KCl	24.74	32.88	3.04	1171.10	2.24
	24.84	33.06	3.02	1171.82	
NaNO <sub>3</sub>	45.71	84.21	1.18	1137.81	1.90
	45.85	84.69	1.18	1138.43	
KNO <sub>3</sub>	20.66	26.04	3.84	1141.23	2.07
	20.82	26.30	3.80	1142.25	
K <sub>2</sub> SO <sub>4</sub>	8.48	9.26	10.79	1176.84	--

*Decomposition by Heat (Dissociation) of Salts in Solution.* (C. R. C. Tiehborne, *Chem. News*, xxiv. 123, 199, 209, 230; xxv. 133.)—Experiments with solutions of ferric chloride, ferric sulphate, chromic sulphate, chrome-alum, ammonia-iron alum, potash-iron alum, ammonia alum, and potash alum (partly in sealed tubes at  $177^\circ$ ), showed that all these compounds are more or less decomposed by heating their aqueous solutions, the ferric salts most easily of all. The solutions of these latter gradually become darker, and when dilute deposit, even below the boiling point, a pregradually become darker, and when dilute deposit, even below the boiling point, a precipitate of a basic salt; while at higher temperatures, under pressure, or in very dilute solutions even under ordinary circumstances, anhydrous ferric oxide may be formed. *Chromic salts* decompose in a similar manner, excepting that the point of decomposition is higher. In solutions of *aluminium salts* it is still considerably higher; these solutions give precipitates at the boiling heat under a pressure of 11 or 12 atmospheres, or even at  $100^\circ$ , if they contain from 50,000 to 60,000 pts. water to 1 pt. of salt.

*Solubility of Mixed Salts at 15.6°, and Specific Gravity of the Solutions.*

Mixture of Salts	Quantity of Salt		Specific gravity of the solution
	in 100 pts. of solution	to 100 pts. of water	
{ KCl	9.62	13.92	1233.74
{ NaCl	21.21	30.65	
{ KNO <sup>3</sup>	15.29	34.53	1478.22
{ NaNO <sup>3</sup>	40.39	91.16	
{ K <sup>2</sup> NO <sup>3</sup>	18.79	32.32	1330.92
{ NaCl	23.03	39.57	
{ K <sup>2</sup> SO <sup>4</sup>	4.99	7.19	1241.51
{ NaCl	25.52	36.71	
{ KCl	0.82	1.39	1329.74
{ NaCl	22.51	38.58	
{ KNO <sup>3</sup>	18.33	31.44	1438.63
{ NaCl	12.65	26.44	
{ NaNO <sup>3</sup>	25.68	53.68	1250.42
{ KNO <sup>3</sup>	13.83	28.92	
{ K <sup>2</sup> SO <sup>4</sup>	3.19	4.69	1250.42
{ KCl	6.88	10.11	
{ NaCl	21.88	32.15	

Solutions of *hydrated salts of cobalt, copper, and nickel* gave the following results:—Neutral aqueous solutions of the chlorides, *e.g.* the light rose-coloured solutions of cobalt chloride, do not change colour when boiled under ordinary atmospheric pressure. But in every case in which a difference of colour is observed between the dry and the hydrated salt, the dehydration may be brought about by increasing the pressure. Of the greatest importance is the observed opposite influence of dilution on salts which decompose, like ferric and chromic salts, with formation of a basic salt, and of those which merely suffer dehydration. In the former the temperature of decomposition is lowered by dilution, in the latter it is raised, as shown by the following table:

Decomposition of Ferric Chloride, with separation of base			Decomposition of Cobalt Chloride, with separation of hydration-water		
Percentage of Hydrated Salt in the solutions	Temperature of decomposition	Colour	Percentage of Hydrated Salt in the solutions	Temperature of decomposition	Colour
50	above 100°	—	50	{ 60° 100	altered blue
10	" 94	—	25	{ 85 135	altered blue
5	" 82	—	10	{ 180 207	altered blue

The decomposition by heat of certain ammonia salts and acetates in aqueous solution has been investigated by H. C. Dibbitts (*Deut. Chem. Ges. Ber.* v. 820). The ammonia salts named in the following table give off ammonia at ordinary temperatures, as well as at the boiling points of their solutions; a solution of the acetate, through which a stream of hydrogen was passed, gave off ammonia even at 0°. The quantity of free ammonia in the distillate is proportional to the concentration of the solution. The proportions of the several salts thus decomposed in solution are given in the following table:

Sodium acetate	0.14	p.c. at 100-102°	Ammonium chloride	0.062	p.c. at 100°
Barium "	0.064	" " 100-101.5	" nitrate	0.072	" "
Lead "	5.0	" " 100	" sulphate	1.1	" "
Silver "	0.72	" " 100	" oxalate	6.7	" "
			" acetate	7.9	" "



In the case of the chloride and acetate of ammonium, which give off acid as well as ammonia, these numbers must be regarded only as maxima.

For Favre a. Valson's experiments on the Dissociation of Crystallised Salts in Solution, see *CHEMICAL ACTION* (pp. 292-304).

For Berthelot's experiments on the state of Acid Salts in Solution, and on the Division of a base in Solution between two Acids, see pp. 286-290.

**Supersaturated Saline Solutions.**—These solutions are usually prepared by leaving a solution saturated while hot to cool in a vessel in which it is protected from the dust of the air. De Coppet (*Compt. rend.* lxxiii. 1324) finds that a supersaturated solution of sodium sulphate is formed when anhydrous sodium sulphate previously heated above  $33^{\circ}$ , and cooled out of contact with the dust of the air, is dissolved in cold water, the salt being added by small quantities at a time to prevent any considerable rise of temperature. By operating in this manner, water may be made to take up a quantity of sodium sulphate five times as great as that which is contained in a solution of the hydrate,  $\text{Na}^2\text{SO}^4 \cdot 10\text{H}^2\text{O}$ , saturated at the ordinary temperature.

In like manner supersaturated solutions of sodium carbonate and magnesium sulphate may be prepared without heating, by the use of anhydrous sodium carbonate and partially dehydrated magnesium sulphate.

On the causes which determine the separation of salts from supersaturated solutions, see Tomlinson (*Proc. Roy. Soc.* xvi. 493; xviii. 533, 536; xx. 41, 109, 342; *Phil. Mag.* [4], xxxvi. 222; xl. 221, 224, 295; xlv. 243; *Chem. Soc. J.* [2], vii. 125; x. 284, 784; xi. 720; *Jahresb. f. Chem.* 1868, 43; 1870, 44; 1871, 36; 1872, 20), Gernez (*Compt. rend.* lxxv. 1705; *Jahresb.* 1872, 20; *Chem. Soc. J.* [2], xi. 720), Van der Mensbrugghe (*Compt. rend.* lxxvi. 45; *Chem. Soc. J.* [2], xi. 721), Liversidge (*Chem. News*, xxii. 90; *Proc. Roy. Soc.* xx. 497; *Chem. Soc. J.* [2], xi. 469).

**SALYLIC ACID.** This name was given by Kolbe a. Lautemann to a supposed isomeric of benzoic acid, the existence of which has, however, not been satisfactorily established (v. 185).

The same name is applied by G. Städeler (*Ann. Ch. Pharm. Suppl.* vii. 159) to two acids, distinguished as  $\alpha$  and  $\beta$ , derived from salicyl,  $\text{C}^1\text{H}^2\text{O}^2$ , by addition of the elements of water.

When salicyl which had stood for twelve years under water, was treated in the dry state with sodium-amalgam, the mass dissolved in water, the solution saturated with carbonic acid, the saligenin thereby produced dissolved out with ether, and the soda solution evaporated to dryness, the residue yielded to alcohol a sodium salt from which sulphuric acid separated an oily acid soluble in hot water and separating therefrom in small crystals. This acid, called by Städeler  $\beta$ -salylic acid, has the composition  $\text{C}^{11}\text{H}^{10}\text{O}^4 = 3\text{C}^1\text{H}^2\text{O}^2 + 2\text{H}^2\text{O}$ . It is sparingly soluble in cold water, easily soluble in alcohol and ether. It melts in the dry state at  $94^{\circ}\text{--}95^{\circ}$ , much more easily under water. A hot aqueous solution of the acid becomes turbid on cooling, from separation of oil-drops, which afterwards turn to crystals resembling benzoic acid, and giving off vapours of similar odour when heated. By slower crystallisation tufts of widely radiating crystals are obtained. The aqueous solution, even when very dilute, acquires a fine violet colour on addition of ferric chloride. The acid appears to be tribasic, but there appears to be considerable difficulty in obtaining its neutral salts.

Recently prepared salicyl similarly treated yielded only saligenin, without a trace of organic acid. This observation led to the suspicion that the  $\beta$ -salylic acid was contained in the salicyl, which had long been under water, and was not produced by the action of the sodium-amalgam; and this proved to be the case, for on dissolving the salicyl in soda, saturating with carbonic acid, agitating with ether, &c., two organic acids were obtained, separable by crystallisation. The one which separated first, called by Städeler  $\alpha$ -salylic acid, had the composition  $\text{C}^1\text{H}^4\text{O}^3 = 2\text{C}^1\text{H}^2\text{O}^2 + \text{H}^2\text{O}$ ; afterwards  $\beta$ -salylic acid crystallised out, but only in small quantity; so that it seems probable that  $\alpha$ -salylic acid is resolved by the action of sodium-amalgam into water and  $\beta$ -salylic acid.

$\alpha$ -Salylic acid forms small, distorted, four-sided prisms with oblique end-face, sometimes shortened into rhombic or six-sided tables. It melts at  $100^{\circ}\text{--}101^{\circ}$ , dissolves easily in alcohol and ether, melts to an oil with water, and when heated alone gives off vapours which excite coughing. Its aqueous solution is not coloured by ferric chloride. It appears to be bibasic, but the neutral salts are difficult to obtain. The silver salt crystallises in small colourless needles, sparingly soluble in cold water, and containing 42.78 p.c. silver instead of 45.88, as required by calculation.

An attempt to prepare the two acids above described by heating salicyl with water did not yield definite results.

**SARANKITE.** See TANTALATES.

**SARSUOLIN,  $\text{C}^{10}\text{H}^{12}$ .** The terpene from elder oil.  
2nd Sup. 3 Z

**SANDAL or SANTAL WOOD OIL.** By destroying the oxidised constituent of this oil with sodium, a small quantity of a hydrocarbon,  $C^{12}H^{18}$ , is separated, rather viscid, slightly soluble in alcohol, having a density of 0.9190, and a refractive index = 1.4867 for the line A. (Gladstone, *Chem. Soc. J.* [2], x. 6).

**SANDBERGITE.** From the analysis of this fahl-ore by Mehrbach (1st Suppl. 1012) Kenngott calculates that if  $Cu^2S$  be separated from  $RS$ , the mineral may be represented by the formula,  $2(4Cu^2S.RS^2) + 4RS.RS^2$  (*Jahrbuch für Mineralogie*, 1871, 179).

**SANTONIC ACID,  $C^{13}H^{10}O^4$**  (Cannizzaro a. Sestini, *Gazzetta chimica italiana*, iii. 241). This acid is formed by the prolonged action of hot alkaline solutions on santonin. 50 grams of crystallised santonin are gradually added, with agitation, to 500 grams of a boiling solution of barium hydrate, whereupon a white amorphous mass is deposited, consisting of the barium salt of santonin (*barium santonite* or *santoninate*). The liquid with the precipitate is boiled for about 12 hours in a flask, with reversed condenser, whereby the santonite is gradually converted into santonic acid, which dissolves, the liquid acquiring a yellow colour. Into this yellow solution, after cooling (and dilution with water, if barium hydrate has crystallised out), a stream of carbonic anhydride is passed as long as a precipitate is formed; the liquid is heated, filtered, and mixed with sulphuric acid, which precipitates barium sulphate, together with the greater part of the santonic acid; and the precipitate is collected on a filter, washed, dried, and treated with alcohol, which dissolves the santonic acid, together with a small quantity of yellow resinous matter. The alcoholic solution is evaporated, the residue treated with ether, and the resulting ethereal solution filtered and evaporated, whereupon it deposits santonic acid in fine large crystals, which have a faint yellowish colour, but may be obtained perfectly colourless by one or two fractional crystallisations from ether. For complete purification the product must be further crystallised by cooling from alcohol diluted with an equal bulk of water.

Santonin acid is colourless, and is not affected by the solar rays, which quickly turn santonin yellow. It is slightly soluble in cold water (100 pts. water at  $17^\circ$  dissolve 0.559 pt.); more soluble in hot water, from which it separates in prismatic crystals; very soluble in ether, still more in alcohol; moderately soluble also in chloroform and glacial acetic acid, very sparingly in carbon sulphide.

The crystals of santonic acid are orthorhombic, exhibiting the combination,  $P_{\infty} : P_{\infty} : OP$ , the macrodome generally predominating. Axes,  $a : b : c = 0.4589 : 1 : 0.6544$ ; angle,  $OP : P_{\infty} = 114^\circ 39'$ ;  $OP : P_{\infty} = 123^\circ 12'$ . Cleavage easy parallel to the faces  $P_{\infty}$ .

Santonin acid melts at  $161^\circ$ – $163^\circ$  (santonin at  $170^\circ$ ), to a colourless liquid, which crystallises to a white mass on cooling, but often exhibits the phenomenon of superfusion. Fused santonic acid undergoes alteration at a temperature not exceeding  $170^\circ$ , turning brown, and giving off an odour like that of some of the pyrogenous products of santonin. With alcohol and caustic potash, it does not give the fine violet-red colour which is characteristic of santonin.

**Santonates.**—Santonin acid has a very decided acid reaction, and decomposes carbonates with brisk effervescence when the solution is heated with them. It is monobasic. The *sodium salt*,  $C^{13}H^{10}NaO^4$ , separates from a solution concentrated to a syrup and placed over sulphuric acid, as an amorphous, transparent, or vitreous mass, having a faint straw-yellow colour; but by open evaporation over the water-bath, it is obtained in radiate or stellar groups of needles. It is deliquescent, very soluble in water and in alcohol; soluble also in ether containing alcohol. The *silver salt*,  $C^{13}H^8AgO^4$ , obtained by precipitating the barium salt with silver nitrate, is white, but alters on exposure to light. It may be washed on a filter with cold water, in which, however, it dissolves somewhat freely. The *barium salt*,  $(C^{13}H^8O^4)_2Ba$ , is very soluble in water, but may be obtained in crystals by evaporating its concentrated solution over sulphuric acid. It is not precipitated from its aqueous solution by alcohol; but on adding a mixture of alcohol with a little ether to its concentrated aqueous solution, it separates in delicate needle-shaped crystals which remain for a long time suspended in the liquid.

H. Hvoslef (*Deut. Chem. Ges. Ber.* vi. 1471) states that he prepared santonic acid by the same process as Cannizzaro a. Sestini, as long ago as 1863. He gives the same formula and basicity for the acid, but finds that it melts at  $171^\circ$ .

The santonates of the heavy metals are, according to Hvoslef, for the most part soluble in boiling alcohol, and the solutions when cooled yield gelatinous masses which gradually crystallise.

The further action of baryta on the solution from which santonic acid has been precipitated by hydrochloric acid yields two bodies, one of which is apparently a sugar. Santonic acid would therefore seem to be a glucoside (Hvoslef).

**SANTONIN**,  $C^{12}H^{10}O^2$ . *Detection in Urine*.—W. G. Smith (*Pharm. J. Trans.* [3], i, 528), finds that the urine of a person who has taken santonin acquires a greenish-yellow colour, immediately changed to red by alkalis. The greenish-yellow colour, which sometimes approaches to a light saffron-yellow, is most easily observed by looking obliquely along the surface of the liquid. The reddening is produced by potash, soda, ammoniac, lime and baryta, but the reaction is most distinct with potash. With acids this urine gives reactions similar to those exhibited by urine containing bile. A small quantity of nitric acid produces in it a transient purple-red colour; sulphuric acid a red-brown colour, gradually changing to a darker brown. This reaction must be borne in mind in testing urine for bile. The reaction with alkali is so distinct, that santonin may with certainty be detected by it in the urine from 10 to 60 minutes after it has been swallowed. After a dose of 6 to 10 grains, the reaction was still perceptible after two days. The red liquid examined by the spectroscope showed that the red, orange and yellow rays were transmitted, whilst the blue end of the spectrum was absorbed. In very dilute solutions, the middle rays only were absorbed, the red and blue being transmitted.

The red colouring-matter may be isolated by lead acetate, and appears to be moderately permanent. It unites with basic lead acetate, and forms a brown precipitate with iron salts. It appeared, therefore, probable that the substance was a weak acid, formed by oxidation of santonin; and, indeed, by heating santonin with nitric acid, a greenish-yellow liquid is formed, which, when treated with an alkali, immediately acquires an orange-red colour, exactly like that which is produced by similar means in urine after ingestion of santonin. This colouring matter, however, is not identical with that separated from the urine, inasmuch as its solution is not precipitated by acetate of lead.

**Santonites**.—This name is applied by Cannizzaro & Sestini (*Gazzetta chimica italiana*, iii, 241) to the metallic derivatives of santonin,  $C^{12}H^{10}RO^2$ , originally called *santonates* by Heldt, who first examined them (v. 190). They are really salts of santoninic acid, and should therefore be called santoninates.

Cannizzaro & Sestini find that when sodium santonite, which, according to Heldt, contains four molecules of crystallisation-water, is heated above  $100^\circ$ , it is converted, by assimilation of the elements of one molecule of water, partly into santonate, partly into a substance having a red colour changing to brown.

**Santonin Bromide**,  $C^{12}H^{10}O^2Br^2$ , is formed on adding bromine to a solution of santonin in bromine, or in glacial acetic acid. It is best prepared by means of the latter solvent, the bromine being added in molecular proportion ( $Br^2 : C^{12}H^{10}O^2 = 160 : 246$ ). After two or three hours the bromine-compound separates in fine, red, needle-shaped crystals, which must be collected on a well-dried double filter, washed four or five times with glacial acetic acid, pressed in the filter between two glass plates, then within several folds of thoroughly dried paper, placed between bricks and squeezed in a press, and finally dried over sulphuric acid or sticks of potash.

This compound dissolves with red colour in ether and in acetic acid; it emits a faint odour of bromine, absorbs water from the air, and quickly alters, yielding the hydrogen bromide and a red-brown, amorphous substance. When heated in the water-bath, it first gives off bromine, then suddenly turns brown, and gives off large quantities of hydrogen bromide. In contact with water, it gives up its bromine in a few seconds, colouring the water yellowish-red. The solution is decolorised by potash, with formation of hydrobromic acid, and a white residue possessing all the properties of santonin.

From these reactions it may be inferred that the red compound is a brominated addition-product of santonin, although, on account of the difficulty of purifying it, the numbers obtained by analysis do not agree very closely with the formula,  $C^{12}H^{10}Br^2O^2$  (35.24 and 35.42 p.c. bromine, instead of the calculated quantity of 39.41).

**Action of Nascent Hydrogen on Santonin**.—Santonin treated with water and sodium amalgam containing 3 p.c. sodium, gradually dissolves, forming a strongly alkaline liquid, which when treated, after cooling, with very dilute sulphuric acid, yields a white flocculent precipitate, which may be washed with cold water, dried by pressure between paper, and finally over sulphuric acid.

This white substance is soluble in ether, very soluble in alcohol, sparingly in water, and separates from these solvents in the amorphous state, with yellow colour and resinous aspect. Between  $80^\circ$  and  $90^\circ$  it becomes somewhat viscid; at  $100^\circ$  it turns yellow, and may be drawn out into threads, becoming hard and friable on cooling; between  $107^\circ$  and  $109^\circ$  it exhibits signs of actual fusion. Towards  $120^\circ$  it gives off slightly acid water, smelling like formic acid; towards  $160^\circ$  a few drops of an acid liquid which reduces silver nitrate; and above  $180^\circ$  a small quantity of oily matter, which solidifies to a white mass on cooling. When dissolved in glacial acetic acid and

treated with bromine, it gives off hydrobromic acid, even when the liquid is cooled, and does not yield any crystalline compound. This reaction indicates that it contains more hydrogen than santonin; that, in fact, it is a hydrosantonin; a view which accords with its mode of formation. It has not, however, been obtained in a state fit for analysis. It forms crystalline compounds with alkalis and alkaline earths (Cannizzaro a. Sestini, *loc. cit.*)

**SANTONINIC ACID**,  $C^{12}H^{10}O^4$  (O. Hesse, *Deut. Chem. Ges. Ber.* vi. 1280). This acid, of which santonin is the anhydride, is isomeric with santonie acid. The so-called santonites are its salts, and it may be obtained in the free state by adding an excess of dilute hydrochloric acid to a cold aqueous solution of the sodium salt, and at once shaking the milky liquid with ether (at higher temperatures santonie acid is formed). From the ethereal solution granular crystals soon separate out, which may be recrystallised from alcohol.

Santoninic acid forms white, rhombic crystals, which are not coloured yellow by exposure to light. It is sparingly soluble in cold water, more freely in boiling water, and readily in alcohol, but not very freely in ether. Its aqueous solution has a strongly acid reaction, and when hot, decomposes the carbonates of sodium and calcium. The santoninates have an alkaline reaction, and are not coloured red by alcoholic potash. When the acid is heated to  $120^\circ$ , it is resolved into santonin and water; the same decomposition is produced by adding sulphuric acid to its aqueous solution; hydrochloric acts in the cold in a similar way, but more slowly, while by adding either of these acids to a hot solution of a salt, santonin is at once precipitated.

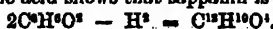
**SANTONOL**,  $C^{12}H^{10}O^2$  (L. Saint-Martin, *Compt. rend.* lxxv. 1190). A monatomic phenol obtained from santonin. When one part of santonin and four parts of zinc are heated in a current of hydrogen, a brownish-yellow liquid is obtained, in which, after some days, needle-shaped crystals begin to form. These are purified by distillation at  $350^\circ$ , when two isomeric bodies neutral to litmus are obtained, the one crystalline and the other liquid, to both of which the name of *santonol* is given. *Crystalline santonol* is similar in appearance to stearin, and melts at  $135^\circ$ . It is insoluble in water, and very soluble in alcohol or ether. Sulphuric acid forms with it a sulpho-conjugated acid, the barium salt of which is soluble. *Santonol* dissolves when it is mixed with a moderate quantity of potash solution, but a large excess of potash gives rise to *potassium santonolate*, which is an oil yielding santonol on treatment with an acid.

*Liquid santonol* is very changeable on exposure to air. Like the solid, with which it is saturated, it is insoluble in water, but soluble in alcohol or ether.

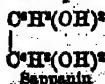
**SAPPANIN**,  $C^{12}H^{10}O^4$  (J. Schreder, *Deut. Chem. Ges. Ber.* v. 572). A crystallisable substance, obtained together with resorcin and a little pyrocatechin, by fusing the commercial extract of sapan wood with caustic soda. It is nearly insoluble in cold water, and separates readily from solution in hot water in crystals containing  $C^{12}H^{10}O^4 \cdot 2H^2O$ . By recrystallisation or by keeping in well-closed vessels, it acquires a faint red colour which is not removed by animal charcoal, but completely by zinc and sulphuric acid. Sappanin has no well-marked characteristics; it is neutral, soluble in alcohol, ether, and boiling water, and insoluble in chloroform, carbon sulphide, and benzene; it gives (in aqueous solution) a deep cherry-red colour with ferric chloride, and a dark grass green, soon becoming brown, with alkaline hypochlorites; bromine-water colours the liquid brown, and when added in excess causes resinous brown-black flakes to separate. Lead acetate gives a yellowish-white precipitate which becomes coloured and decomposed on drying. Ammoniacal silver-solution and Fehling's copper-solution are reduced on warming. Sappanin distils for the most part unaltered; nitric acid converts it into styphnic acid; melting caustic potash and nascent hydrogen produce no change.

Acetyl chloride acts readily on sappanin at ordinary temperatures, giving a product which is crystallisable from hot alcohol, and hardly soluble in water; this substance gives no colour with ferric chloride or hypochlorites, and appears to be tetracetylsappanin.

The production of styphnic acid shows that sappanin is a resorcin-derivative:—



It is perhaps related to resorcin in the same manner as diphenyl to benzene:



**SARCINE**,  $C^8H^8N^2O$ . This base is formed from carnine by the action of bromine-water (p. 270).

When sarcine is heated with fresh chlorine-water and a trace of nitric acid till the evolution of gas which takes place at first has slackened, and the liquid is then evaporated on the water-bath, a residuo is obtained which, when exposed under a bell-jar to an atmosphere containing ammonia, acquires a dark rose-red colour.

**SARCOLACTIC ACID.** See LACTIC ACID (p. 719).

**SARCOSINE.** *Reaction in the Animal Organism.*—When to a well-fed dog there was given, in addition to his ordinary food, a quantity of sarcosine containing nitrogen equal in amount to that which was daily excreted in the urine, the urea and uric acid disappeared completely from the urine, and instead of them, there were obtained: (1) splendid transparent, colourless, tabular crystals of a body having the composition  $\text{H}^2\text{NCO}-\text{N}\begin{Bmatrix} \text{CH}^3 \\ \text{CH}^3\text{CO}^2\text{H} \end{Bmatrix}$ ; that is to say, urea having the two hydrogen-atoms attached to one of its nitrogen-atoms replaced by methyl and acetoxy, or sarcosine having a carbamic acid residue attached to its nitrogen; (2) An acid,  $\text{H}^2\text{NSO}^2\text{N}\begin{Bmatrix} \text{CH}^3 \\ \text{CH}^3\text{CO}^2\text{H} \end{Bmatrix}$ , formed by the combination of sulphamic acid and sarcosine, with elimination of water.

The formation of these substances may perhaps be explained as follows:—1. The sarcosine, in its passage through the animal organism, meets with the carbamic acid group, and unites therewith, with elimination of water, to form the substituted urea. If ammonia were to come in contact with this group, ordinary urea would be formed instead of sarcosine. 2. The sulphuretted acid above mentioned is formed by the union of the sarcosine with sulphuric acid. Under normal circumstances, the sulphamic acid pre-existing in the albumin yields sulphuric acid and ammonia, the latter of which unites with carbamic acid to form urea. Other bodies are formed at the same time (O. Schulzon, *Deut. Chem. Ges. Ber.* v. 578).

**SCAPOLITE.** A greenish-white translucent mineral from Attleborough, Bucks Co., Pennsylvania, has been recognised by Leeds (*Chem. News*, xxii. 73) as Scapolite (Nebegito). It occurs in granular limestone in imperfectly developed crystals, together with pyroxene, graphite, sphene, and phlogopite. Analysis gave:

$\text{SiO}^2$	$\text{AlO}^2$	$\text{FeO}^2$	$\text{MgO}$	$\text{CaO}$	$\text{Na}^2\text{O}$	$\text{K}^2\text{O}$	$\text{H}^2\text{O}$
47.47	27.61	trace	1.20	17.59	3.05	1.40	1.48 = 99.61.

**SCHHEELITE.** A monograph on the morphological and paragenetic relations of this mineral has been published by Max Bauer (*Pogg. Ann.* cxliii. 452; *abstr. Jahrb. f. Mineralogie*, 1871, 879; *Jahresb. f. Chem.* 1871, 1169).

The occurrence of scheelite at Domodossola in Piedmont is described by Le Nove Foster (*Jahrb. f. Mineralogie*, 1870, 233).

**SCOLEZITE.** Kenngott (*ibid.* 430) has examined the behaviour of Icelandic scolezite with acids. The powder, which has a very faint alkaline reaction, forms a jelly with hydrochloric, nitric, and sulphuric acids, and with the last-mentioned acid, macroscopic crystals of gypsum.

Igelström (*ibid.* 1869, 1223) found in scolezite occurring in white divergent needles in the diabase porphyry of Lundörsfjäll in Sweden:

$\text{SiO}^2$	$\text{AlO}^2$	$\text{CaO}$	$\text{H}^2\text{O}$
46.56	25.75	15.00	13.30 = 100.61.

**SEA-WATER.** On the estimation of Carbonic acid in sea-water, see p. 561.

On the detection of Gold in sea-water, see p. 574.

On the detection and estimation of Iodine in sea-water, see p. 670.

**SEBIC or SEBACIC ACID.** On the formation of Cetyl Alcohol by the distillation of this alcohol with caustic baryta, see p. 277.

**SEDUM.** The Biting Stonecrop (*Sedum acre*) has been examined chemically by E. Mylius (*Arch. Pharm.* [3], i. 97). The dried and powdered plant, treated successively with ether, alcohol, cold, hot, and acidulated water, yielded—besides wax, chlorophyll, and other vegetable matters—rutin, and a small quantity of a peculiar alkaloid, amorphous, and forming very soluble salts. The rutin, by boiling with dilute acid, yielded quercetin and a sugar which reduced an alkaline cupric solution.

*Sedum calcarum* contains, according to Baudrimont (*Compt. rend.* lxxiv. 877), 87.81 p.c. water and volatile matter, 7.76 organic matter, and 3.11 mineral matter.

**SEEBACHITE.** This name is given by Max Bauer (*Jahrb. f. Mineralogie*, 1872, 739) to a mineral from Richmond in Victoria, formerly regarded as Herschelite (*Jahresb. f. Chem.* 1870, 1301; 1871, 1159). It agrees with Herschelite in crystalline form, but differs from it considerably in chemical composition (iii. 150).

An analysis by Kerl gave the values A, which Bauer refers to the formula  $\{2(\text{Na}^+\text{O} \cdot 2\text{Al}^+\text{O}^{\cdot} \cdot 7\text{SiO}^{\cdot} + 12\text{H}^+\text{O})\}$ , requiring the values B.

	$\text{SiO}^{\cdot}$	$\text{Al}^+\text{O}^{\cdot}$	$\text{CaO}$	$\text{Na}^+\text{O}$	$\text{K}^+\text{O}$	$\text{H}^+\text{O}$	
A. . .	43.7	21.8	8.5	3.5	trace	22.2	= 99.7
B. . .	43.6	21.6	8.5	3.7	—	22.6	= 100

Konngott designates the same mineral as Levyn.

**SEEDS.** On the effect of various substances in promoting or retarding the Germination of seeds, see A. Vogel (*N. Rep. Pharm.* xx. 132; *Chem. Soc. J.* [2], ix. 748). On the influence of Germination on the amount of Fat in seeds, see A. Müntz (*Ann. Chim. Phys.* xxii. 472; *Chem. Soc. J.* [2], ix. 1207); also A. Vogel (*N. Rep. Pharm.* xx. 693; *Chem. Soc. J.* [2], x. 317).

On the percentage of Fat in Oil-seeds, see p. 506 of this volume.

Apparatus for the Extraction of Oil from seeds: see H. Vohl (*Dingl. pol. J.* cci. 171).

**SELAGITE.** A dark-coloured micaceous volcanic rock from Monte Catini. It occurs imbedded in mica, has a specific gravity of 2.789, hardness 4.5, and contains:

$\text{SiO}^{\cdot}$	$\text{Al}^+\text{O}^{\cdot}$	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}^+\text{O}$	$\text{K}^+\text{O}$	$\text{P}^+\text{O}^{\cdot}$
44.5	1.7	37.3	1.4	14.0	trace		1.1 = 100

(E. Bechi, *Sill. Am. J.* [4], xlix. 401).

**SELENIOTRITHIONIC ACID**,  $\text{H}^+\text{SeS}^+\text{O}^{\cdot}$ . See TRITHIONIC ACID, under SULPHUR.

**SELENITE.** On the crystalline form of this mineral, see F. Schrauf (*Jahrb. f. Mineralogie*, 1871, 881).

**SELENIOWALERALDEHYDE**,  $\text{C}^+\text{H}^+\text{Se}$ . See VALERALDEHYDE.

**SELENIUM.** *Occurrence.*—Ch. Violette (*Compt. rend.* lxx. 729) has found selenium in copper, probably from Chilo. To detect the selenium the copper was oxidised in a muffle, and the oxide, heated to redness in a tube, was subjected for several hours to a stream of pure dry air. The selenium was then deposited on the colder part of the tube in the form of a white ring of selenious oxide.

The occurrence of selenium in sulphuric acid prepared from seleniferous pyrites is described by J. Personne (*ibid.* lxxiv. 1109), Lamy (*ibid.* 1285), and Scheurer-Kestner (*ibid.* 1286); see also *Chem. Soc. J.* [2], x. 595.

On the Refraction and Dispersion of selenium, see LIGHT (p. 741).

*Absorption-spectrum.*—When selenium is heated in a porcelain tube by a series of gas jets, whilst a ray of white light is passed through the tube, the spectrum is found to be gradually extinguished from the violet up to the red, without any appearance of black lines; on raising the temperature considerably, the spectrum becomes brighter, and bundles of black lines appear, furrowing the blue and violet. This spectrum resembles that of selenious anhydride, but as it was obtained in an atmosphere of dry carbonic anhydride, the formation of selenious anhydride is impossible.

Vapour of selenious chloride gives an absorption-spectrum of lines which extend from the green to the violet.

Vapour of selenious bromide produces a system of lines almost equidistant when observed in a thickness of 10 centimeters (Gernez, *Compt. rend.* lxx. 1100).

On the spectrum of selenium, see further, Salet (*Compt. rend.* lxxiii. 1145; *Chem. Soc. J.* [2], ix. 1145), and Ditto (*Compt. rend.* lxxiii. 622; *Chem. Soc. J.* [2], ix. 1146).

*Action of Light on the Electric Resistance of Selenium.*—The electric conductivity of crystalline selenium varies with the degree of light to which it is exposed. A bar of selenium having been enclosed in a box and the resistance measured in the usual manner, on opening the box suddenly, and exposing the selenium to daylight, the resistance fell instantaneously and considerably; on exposing it in like manner to full sunshine, the resistance was so greatly diminished that it was less by one-half than the measurement taken in darkness.

The bar was also exposed to the rays of the solar spectrum successively. The least resistance was observed in the extreme red rays, and the greatest in the violet and blue rays; it will be noticed, therefore, that the locus of the maximum heat-rays is nearly coincident with the point of minimum resistance.

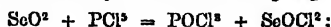
The spectrum of the electric light produced a very feeble effect, but the phenomena were identical with those produced by the solar spectrum.

This variation in the electric resistance of selenium is not due to any change in the temperature of the bar (Lieut. Sale, R.E., *Proc. Roy. Soc.* xli. 233).

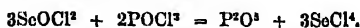
On the Heat of Combination of Selenium with Oxygen and Hydrogen, see *Heat* (pp. 613, 615).

On the Heat of Neutralisation of Selenious and Selenic acids, see *1st Suppl.* 1086.

**Chlorides** (Michaelis, *Jenaische Zeitschr.* vi. 86). When selenious anhydride is placed in contact with phosphorus pentachloride, great heat is evolved, and the mass gradually liquefies; but if further heated it again becomes solid. The first reaction is analogous to that of the pentachloride on sulphurous anhydride, the products being selenium oxychloride or selenyl chloride, and phosphoryl chloride:



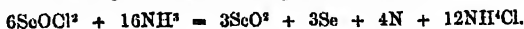
and the phosphoryl chloride then acts further on the selenyl chloride, forming phosphoric anhydride and selenium tetrachloride:



This last reaction is in fact produced when selenyl chloride is directly heated with phosphoryl chloride. The action of phosphorus pentachloride on selenious anhydride affords a quick and easy method of preparing the tetrachloride of selenium.

Selenyl chloride boils at  $179.5^\circ$  (corr.), not at  $220^\circ$ , as stated by Weber (v. 233), and solidifies below  $0^\circ$  to a colourless crystalline mass, which begins to melt at  $10^\circ$ . Sp. gr. = 2.443 at  $13^\circ$ .

Ammonia acts on selenyl chloride according to the equation:

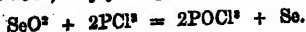


When phosphorus trichloride is added by drops to selenyl chloride in a cooled vessel, selenium tetrachloride crystallises out, and diselenium dichloride is formed at the same time, the liquid turning red:



**Hydride.** *Hydrogen Selenide.* *Selenhydric acid*,  $\text{H}_2\text{Se}$ . *Formation and decomposition.*—Hautefeuille showed (*Compt. rend.* lxiv. 608) that selenium and hydrogen unite directly at about  $440^\circ$ . According to A. Ditte (*ibid.* lxxiv. 980) the quantity of hydrogen selenide thus formed is a function of the temperature. It increases from  $250^\circ$  to  $520^\circ$ , and decreases regularly from the latter point to  $700^\circ$ . If the application of heat be limited to the part of the tube containing the selenium, as much hydrogen selenide is formed as when the whole of the tube is heated; but selenium is deposited on the colder part in beautiful shining crystals, which continue to increase as long as there is any selenium remaining in the heated part of the tube. This apparent volatilisation of the selenium is due, in fact, to decomposition of hydrogen selenide previously formed. The quantity of the gas thus decomposed is greater as the temperature to which the cooler part of the tube has fallen is nearer to  $270^\circ$ . The decomposition of hydrogen selenide begins, though very slowly, at  $150^\circ$ , is considerable at  $270^\circ$ , and diminishes slowly above that temperature, attaining a minimum at  $520^\circ$ , and increases again at higher temperatures. That the deposition of the crystallised selenium in the experiment above described is really due to decomposition of hydrogen selenide, and not to simple volatilisation of the selenium, is proved by substituting for the hydrogen a gas which does not act on selenium; in this case the upper part of the tube merely becomes coated with a red opaque film.

**Oxides and Oxygen Acids.** *Selenious Anhydride*,  $\text{SeO}_2$ .—When this compound is brought in contact with phosphorus trichloride, both bodies become hot and red, but undergo no further alteration in the cold. Heated together in a sealed tube to  $100^\circ$  and afterwards to  $110^\circ$ , they yield phosphoryl chloride and free selenium:



In one experiment, in which the temperature was raised to  $130^\circ$ , the phosphoryl chloride acted on the still unreduced selenious oxide, in such a manner as to produce selenium tetrachloride, which was then reduced by the free selenium to diselenium dichloride (Michaelis, *Jenaische Zeitschrift*, vi. 93).

**Selenates.**—*Ammonium Selenate*,  $(\text{NH}_4)_2\text{SeO}_4$ , forms monoclinic crystals having the axes  $a : b : c = 1.2065 : 1 : 1.908$ , and angle  $b \wedge c = 64.27^\circ$ . The observed forms (expressed in Miller's notation) are 001, 100, 102, 011, 111,  $\bar{1}\bar{1}\bar{1}$ . The salt has the same composition as the rhombic ammonium selenate, isomorphous with the sulphate, described by v. Lang (*Wien. Akad. Ber.* [2. Abth.], xlv. 109), with which, however, it has no crystallographic relation (Topsoe, *ibid.* lxxvi. 5).

**Glucinum Selenate,  $\text{GSeO}_4 + 4\text{H}_2\text{O}$ , crystallises in the rhombic system;  $a : b : c = 0.9802 : 1 : 0.90275$ . Observed forms, 011, 101, 021, 111, 001. It is**

analogous in composition to the sulphate  $\text{GSO}^4 + 4\text{H}^2\text{O}$ , which crystallises in the quadratic system, and when mixed solutions of these two salts are left to evaporate slowly, mixed crystals are obtained, quadratic if 7.33 or more atoms of sulphuric acid are present to 1 at. selenic acid, rhombic in the contrary case (Topsoë, *loc. cit.*)

**Sulphides.** (Bettendorff a. vom Rath, *Pogg. Ann.* cxxxix. 329.) When selenium and sulphur are fused together in the most various proportions, the fused mass left to solidify partially, and the remaining liquid portion poured off, no crystalline products are obtained, the fused masses remaining pasty and completely destitute of crystalline structure. By solution in carbon sulphide, however, in which they gradually dissolve, they may be slowly brought into the crystalline state. This metamorphosis takes place in a short time at  $100^\circ$ , and more quickly as the proportion of sulphur in the compound is larger.

The following products were obtained by fusing 1 at. selenium with 2, 3, and 4 at. sulphur, heating the mixture for some time to  $100^\circ$ , dissolving it in carbon sulphide, and evaporating the solutions. The masses which contained 1 at. selenium to 2 and 3 at. sulphur yielded in this manner monoclinic crystals from 2 to 4 mm. long, which were previously observed by Rathke, but described by him as rhombic (1st *Suppl.* 1015). At first there separated deep red crystals rich in selenium; afterwards light orange-coloured crystals containing but a small proportion of that element; and between these occurred crystallisations varying in colour as well as in composition.

The solution of the fused mass obtained with 4 at. sulphur to 1 at. selenium deposited, on evaporation, first small monoclinic crystals of the colour of chromic acid, then others having the colour of acid potassium chromate, and finally a mixture of lighter-coloured crystals with numerous large orange-red rhombic octohedrons, agreeing nearly in composition with the formula  $\text{SeS}^4$ .

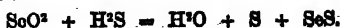
The products which approximated in composition to the formulæ  $\text{SeS}^3$  and  $\text{SeS}^2$  yielded, when their solutions were left to evaporate, first deposits comparatively rich in selenium, afterwards deposits containing more sulphur, and could not therefore be recrystallised without decomposition. The same is the case with the rhombic octohedrons. On dissolving them in carbon sulphide they become opaque, indicating that they pass into a different modification in dissolving. The solution first deposits prismatic crystals comparatively rich in selenium, then follow the orange-red rhombic crystals of various shades of colour, and lastly pure sulphur separates.

With exception of the rhombic octohedrons just mentioned, all the crystals examined by Bettendorff and vom Rath, and obtained from mixtures of sulphur and selenium in the proportions,  $\text{Se} : \text{S}^2, \text{Se} : \text{S}^3, \text{Se} : \text{S}^4$ , have the same form and belong to the monoclinic system, with the following axial ratios:

Clinoïdagonal	Orthoïdagonal	Principal axis
1.0546	1	0.7146

Angle of inclined axes  $= 91^\circ 43' 35''$ . Combination  $\infty\text{P}2. (\infty\text{P}\infty) - \text{P.P.} (\frac{1}{2}\text{P}\infty)$ . Angle  $\infty\text{P}2 : \infty\text{P}2 = 124^\circ 22'$ ;  $-\text{P} : -\text{P} = 119^\circ 30'$ ;  $-\text{P} : \infty\text{P}2 = 132^\circ 35'$ . They also form twins (like those of gypsum) with the twin-plane  $-\text{P}\infty$ , which does not occur as a crystal-face. The rhombic octohedrons, which have nearly the composition  $\text{SeS}^3$ , exhibit the form and angles of rhombic sulphur.

Ditte (*Compt. rend.* lxxiii. 625, 660) has obtained a crystallised selenium sulphide,  $\text{SeS}$ , by saturating a very dilute solution of selenious acid, cooled to a temperature between  $5^\circ$  and  $0^\circ$ , with hydrogen sulphide previously passed through a bottle filled with ice. The compound then separates as a fine lemon-yellow powder, which, after being well washed and dried in a vacuum, may be brought into the crystalline state by moistening it with a small quantity of carbon sulphide. Crystallisation then begins on the surface, and in a few days the entire precipitate is converted into crystals, while the carbon sulphide becomes saturated with sulphur. This saturated liquid is decanted and replaced by fresh carbon sulphide, the latter poured off after a few seconds, and the product washed, first with pure benzene, then with alcohol. Its formation is represented by the equation:



Selenium sulphide thus prepared forms small, shining, transparent, orange-yellow laminae, of sp. gr. 5.056 at  $0^\circ$ , 3.035 at  $52^\circ$ . The expansion-coefficient between these limits is 0.00014176; the specific heat 0.1274. When heated it melts, and gives off first sulphur-vapour, then mixed vapours of sulphur and selenium. It is insoluble in water and in ether, but dissolves in carbon sulphide. In contact with absolute alcohol it blackens, and is gradually resolved into its constituents.

**SENNA.** See CATHARTIN (p. 270); also *Chem. Soc. J.* [2], ix. 1068.

**SERICIC ACID.** An acid prepared from silk in the same manner as leucogenic acid from wool (p. 724). By evaporation of its aqueous solution it is obtained as a



yellowish, translucent, uncrystallisable, deliquescent mass, soluble in ether and in alcohol. From the analysis of its barium salt it appears to have the composition  $C^{20}H^{20}NO^{14}$  (P. Champion, *Compt. rend.* lxxii. 330).

**SERICITE.** This mineral, from the Taunus range in Western Germany, regarded by List as identical with damourite (v. 235), is, according to v. Lasaulx (*Jahrb. f. Mineralogie*, 1872, 851), a mixture of several compounds.

**SERPENTINE.** S. Meunier (*Compt. rend.* lxxiv. 1325) has examined a number of grey serpentines from the Alps, Brazil, the Grecian Archipelago, &c., and finds them to be composed of magnetic iron ore, augite, olivin, and a hydrated silicate of magnesium. The entire analysis of a specimen from which the several varieties examined did not differ materially, yielded the following numbers:

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	MgO	CaO	FeO	H <sup>2</sup> O	Sp. gr.
39.90	1.25	38.10	2.00	6.42	11.60 = 90.27	2.37-2.52

Proximate analysis yielded 0.79 p.c. magnetic iron ore and 0.80 undecomposable silicate (augite); the rest was decomposable, and could be separated by treatment with alkalis into an anhydrous mineral (olivine) and a hydrated mineral. These results were confirmed by microscopic examination.

Respecting Meunier's views of the relation of serpentine to meteorites, see p. 793.

A serpentine from the Timbertop mountain, Victoria, Australia, analysed by C. Newbery (*Jahrb. f. Mineralogie*, 1871, 464), gave:

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	MgO	H <sup>2</sup> O
39.9	8.2		36.8	15.4 = 100.3.

Rocks allied to the serpentine group, from North Tyrol and Carinthia, have been analysed by R. v. Drosche (*ibid.* 1871, 322; *Jahresb. f. Chem.* 1871, 1205).

**SILICA.** SiO<sup>2</sup>. *Separation from Aqueous Solutions.*—When a solution of sodium silicate is strongly heated in sealed glass tubes, the glass is attacked layer by layer, and silica is dissolved, forming a more acid sodium silicate, which, on cooling, deposits free silica in nodules. The glass, by losing silica, is converted layer by layer into a more basic silicate, which, by taking up water, is ultimately transformed into a stratified zeolitic substance. At about 180° and above, free silica separates from aqueous alkaline solutions in the form of quartz; below 180° in that of tridymite; at still lower temperatures as crystallised, and finally as amorphous hydrate of silica. At ordinary or slightly higher temperatures, and under ordinary pressure, quartz is not formed under any circumstances (O. Maschke, *Pogg. Ann.* cxlv. 549; cxlvi. 90).

According to Rammelsberg (*Deut. Chem. Ges. Ber.* v. 1006), silica, as it is obtained in the analysis of silicates, is, after prolonged ignition, insoluble in a concentrated solution of potassium or sodium carbonate. This ignited silica has a specific gravity of 2.3, and must therefore have passed into the crystallised state of tridymite.

**Hydrates.** Silica, separated from alkali-silicates (or from Wollastonite), contains, after drying over sulphuric acid, from 4.5 to 4.7 p.c. water; after drying at 100°-140°, it contains 4 to 5.7 p.c. water. These numbers represent hydrates  $nSiO^2 + aq$ , in which  $n$  lies between 4 and 8. Air-dried silica does not contain any constant amount of water. Dry dusty silica contains from 36 to 13 p.c. water, or has a composition between  $SiO^2 + 2aq$ , and  $2SiO^2 + aq$ . Between these limits quantities equal to 23 and 15 p.c. water are the most frequent, or hydrates containing  $SiO^2 + aq$ , and  $3SiO^2 + 2aq$  (Rammelsberg).

J. Gottlieb (*J. pr. Chem.* [2], vi. 185) finds that pure silica (prepared from silicofluoric acid), dried at 100° in air freed from moisture by standing over oil of vitriol, contains 4.47 p.c. water, which is nearly the same as that contained in silica dried in ordinary air at 130°-140°. Between 180° and 200°, the quantity diminishes to 4.18 p.c.

**Solubility in Ammonia.**—Pribram (*Zeitschr. anal. Chem.* vi. 119) found that silica in all its states is more or less soluble in aqueous ammonia (1st *Suppl.* 1017). These observations have been confirmed by Souchay (*Zeitschr. anal. Chem.* 1872, 182). Gelatinous silica, in the very loose state in which it is obtained by mixing a dilute solution of water-glass with hydrochloric acid to acid reaction, and then washing it and thoroughly, dissolves at first very easily in aqueous ammonia (of 0.96 sp. gr., and 9.75 p.c. NH<sup>3</sup>); on continually adding silica, the liquid becomes turbid, and at last attains a state intermediate between solution and suspension. After filtration, it was found to contain in one experiment 1 gram of silica to 86.5 pts. of aqueous ammonia, in another 1 to 156. Pribram found 140. Silica prepared as above, and dried at 100°, till its weight became constant, required for solution from 252 to 271, mean 261.6 pts.,

aqueous ammonia to 1 pt. silica. One part of ignited silica dissolved in 280 pts.; 1 pt. silica in the form of rock-crystal, in 12097 pts. aqueous ammonia.

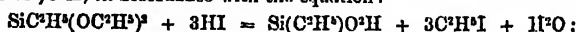
On the action of silica on sodium carbonate at high temperatures, see Maillard (*Compt. rend.* lxxv. 472; *Chem. Soc. J.* [2], xi. 243; *Jahresb. f. Chem.* 1872, 230).

**SILICATES.** To estimate the alkalis in a silicate, J. Lawrence Smith decomposes it by ignition with pure calcium carbonate and sal-ammoniac. For the details of the process, see *Ann. Ch. Pharm.* cliv. 82; *Sill. Am. J.* [3], i. 269; *Chem. News*, xxiii. 222, 234; *Jahresb.* 1871, 914.

**SILICIC ETHERS.** A. Ladenburg (*Ann. Ch. Pharm.* clxiv. 300) has published an elaborate research on the reduction-products of silicic ether,  $\text{Si}(\text{OC}^2\text{H}^5)^4$ , and their derivatives. By the joint action of *zinc-ethyl* and *sodium* on this ether, the following products are obtained:

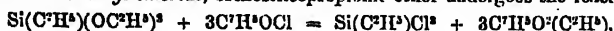
		Boiling point
Orthosilicopropionic ether	$\text{Si}(\text{C}^2\text{H}^5)(\text{OC}^2\text{H}^5)^3$	168.5°
Silicodiethyl ether	$\text{Si}(\text{C}^2\text{H}^5)^2(\text{OC}^2\text{H}^5)^2$	169°
Silicotriethyl or Silico- heptylic ether	$\text{Si}(\text{C}^2\text{H}^5)^3(\text{OC}^2\text{H}^5)$	155.5°
Silicon-ethyl	$\text{Si}(\text{C}^2\text{H}^5)^4$	153°
Silicoheptylic hydride	$\text{Si}(\text{C}^2\text{H}^5)^3\text{H}$	107°

1. *Orthosilicopropionic Ether*,  $\text{Si}(\text{C}^2\text{H}^5)(\text{OC}^2\text{H}^5)^3$ , is produced in this manner much more readily than by the process originally described, viz., treatment of the chloride,  $\text{SiCl}(\text{OC}^2\text{H}^5)^3$ , with zinc-ethyl and sodium (1st *Suppl.* 1020). When warmed with hydriodic acid of boiling point 127° it decomposes, producing silicopropionic acid,  $\text{Si}(\text{C}^2\text{H}^5)(\text{OC}^2\text{H}^5)^3$ , in accordance with the equation:



this is, in fact, the most convenient way of preparing silicopropionic acid.

Heated with *benzoyl chloride*, orthosilicopropionic ether undergoes the reaction:



ethyl benzoate and silicopropionic trichloride (silicon-ethyl trichloride) being produced. This latter has not been obtained perfectly pure; it boils at about 100°, and is decomposed by moist air; water or aqueous ammonia produces hydrogen chloride and silicopropionic acid.

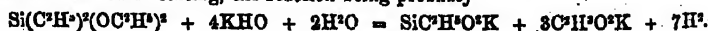
*Phosphorus pentachloride* appears to act on orthosilicopropionic ether, in accordance with the equation:



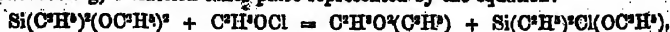
a remarkable action, inasmuch as bodies containing  $\text{OC}^2\text{H}^5$ , associated with carbon, are for the most part not attacked by phosphorus pentachloride (Henry, *Deut. Chem. Ges. Ber.* 1869, 664).

The compound,  $\text{Si}(\text{C}^2\text{H}^5)(\text{OC}^2\text{H}^5)^2\text{Cl}$ , passed over between 148° and 163°, but could not be freed from phosphorus oxychloride, even by repeated fractional distillation.

2. *Silicodiethyl Ether*,  $\text{Si}(\text{C}^2\text{H}^5)^2(\text{OC}^2\text{H}^5)^2$ , boils at 165.8°, has the specific gravity 0.8752 at 0°, and the vapour-density 173.9 (calculated 176); it is stable in the air, insoluble in water, soluble in alcohol and in ether; unlike orthosilicopropionic ether, it does not yield silicopropionic acid by the action of concentrated sulphuric acid, and is not attacked by alcoholic ammonia; it is acted on by concentrated potash-ley only after several hours' heating, the reaction being probably



When silicodiethyl ether and *acetyl* or *benzoyl chloride* are heated together to 200° in a sealed tube in the proportions denoted by the following formulae (the former slightly preponderating) a reaction takes place represented by the equation:



silicodiethyl chloroethylin being formed, which boils between 146° and 148°, and is changed by contact with water into a viscid oil free from chlorine. If, however, two molecules of acetyl or benzoyl chloride and one of silicodiethyl ether are heated to 260°, silicodiethyl chloride,  $\text{Si}(\text{C}^2\text{H}^5)^2\text{Cl}_2$ , is produced, boiling between 128° and 130°:



The vapour of this body mixed with air is explosive. Water decomposes it, forming hydrogen chloride, and a syrupy substance which contains no chlorine; this is silicodiethyl oxide,  $\text{Si}(\text{C}^2\text{H}^5)^2\text{O}$ ; it may be more conveniently prepared by the

action of aqueous hydriodic acid (boiling at  $127^{\circ}$ ) upon silicodiethyl ether, according to the equation:



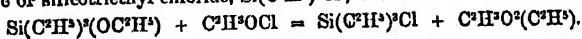
It is a thick syrup, distilling unchanged above the boiling point of mercury, not solidifying at  $-15^{\circ}$ ; it is insoluble in water, difficultly soluble in alcohol, and readily soluble in ether.

From its formula and origin this body appears to be diethyl ketone,  $\text{CO}(\text{C}^2\text{H}^5)^2$ , having its carbon replaced by silicon; unlike carbon ketones, however, it does not combine with unscent hydrogen to form a secondary alcohol; moreover it yields silicopropionic acid on boiling for a day with concentrated soda-ley, whereas diethyl ketone yields only acetic acid by oxidation (Chapman a. Smith). It forms a notable exception to Mendelejoff's rule that silicon-compounds boil at a lower temperature than the corresponding carbon-compounds, as do also the following bodies:—

	Boiling point		Boiling point
$\text{Si}(\text{OC}^2\text{H}^5)^4$	166.5°	$\text{C}(\text{OC}^2\text{H}^5)^4$	128°
$\text{Si}(\text{C}^2\text{H}^5)^3\text{OH}$	154.0°	$\text{C}(\text{C}^2\text{H}^5)^3\text{OH}$	141°
$\text{Si}(\text{C}^2\text{H}^5)^3\text{H}$	107°	$\text{C}(\text{C}^2\text{H}^5)^3\text{H}$	96°
$\text{Si}(\text{CH}^3)^4$	30°	$\text{C}(\text{CH}^3)^4$	9°

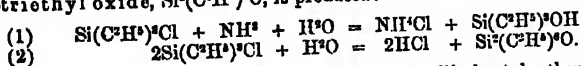
3. *Silicotriethyl Ether* or *Silicoheptylic Ether*,  $\text{Si}(\text{C}^2\text{H}^5)^3(\text{OC}^2\text{H}^5)$ , boils at  $163^{\circ}$ , and has the specific gravity 0.8393 to 0.8414 at  $0^{\circ}$ , and the vapour-density  $161.6^{\circ}$  (calculated  $160^{\circ}$ ); it is stable in the air, soluble in ether and alcohol, and insoluble in water. It is not attacked by alcoholic ammonia, or by aniline at  $250^{\circ}$ , but is decomposed by water at that temperature; it is soluble in concentrated sulphuric acid, wherein it differs from silicon-ethyl.

Acetyl chloride acts on silicotriethyl ether at  $180^{\circ}$ , producing silicoheptyl chloride or silicotriethyl chloride,  $\text{Si}(\text{C}^2\text{H}^5)^3\text{Cl}$ ; thus:

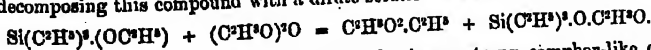


Silicoheptyl chloride is a colourless liquid, which fumes in the air, and burns with a green-edged flame, leaving a white residue. It has a pungent camphorous odour, boils at  $143.5^{\circ}$ , and has a specific gravity of 0.9249 at  $0^{\circ}$ . It is slowly decomposed by water; absolute alcohol appears not to act upon it in the cold, whereas silver nitrate immediately decomposes it with separation of silver chloride. It does not act on mercuric cyanide even at  $270^{\circ}$ , neither can its chlorine be replaced by hydrogen (by treatment with sodium-amalgam and glacial acetic acid).

With aniline, silicoheptyl chloride yields aniline hydrochloride. On dropping it into aqueous ammonia, triethyl-silicol, silicoheptyl alcohol, or silicoheptyl hydroxide,  $\text{Si}(\text{C}^2\text{H}^5)^3\text{OH}$ , separates out nearly pure, provided that the liquid has not been allowed to become hot and acid; in the contrary case silicoheptyl oxide or silicotriethyl oxide,  $\text{Si}^2(\text{C}^2\text{H}^5)^4\text{O}$ , is produced:



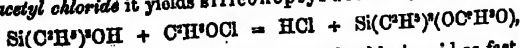
Triethyl-silicol is more easily produced by heating silicoheptyl ether with acetic anhydride to  $250^{\circ}$ , whereby silicoheptyl-acetic ether,  $\text{Si}^2(\text{C}^2\text{H}^5)^4\text{O.C}^2\text{H}^3\text{O}$ , is formed, and decomposing this compound with a dilute solution of sodium carbonate:



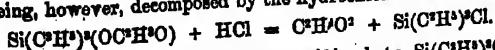
Triethyl-silicol is a colourless viscid liquid, having a strong camphor-like odour, burning with a bright flame, and leaving a residue of silica. It is insoluble in water, slightly soluble in aqueous sodium carbonate, and miscible with alcohol and ether. Boiling point,  $164^{\circ}$ . Sp. gr. = 0.8700 at  $0^{\circ}$ . Determinations of the vapour-density gave for the molecular weight the numbers 134.8 and 124.3 (calc. 132).

Triethyl-silicol exhibits alcoholic characters, as shown by the following reactions:

A. With acetyl chloride it yields silicoheptyl acetate; thus:

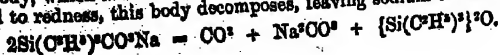


the product being, however, decomposed by the hydrochloric acid as fast as formed:—



B. Sodium evolves hydrogen, giving sodium silicolate,  $\text{Si}(\text{C}^2\text{H}^5)^3\text{ONa}$ .

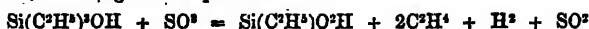
C. An ethereal solution of this latter yields, on passing carbon dioxide into it, an amorphous body, which is silicoheptyl-sodium carbonate,  $\text{Si}(\text{C}^2\text{H}^5)^3\text{O.CO.ONa}$ . When heated to redness, this body decomposes, leaving sodium carbonate; thus:



D. *Hydriodic acid*, boiling at 127°, acts on triethyl-silicol at 200°, forming ethane and silicodiethyl oxide:



E. *Oxidising agents*, such as *chromic* and *permanganic acids*, have no action on triethyl-silicol; Nordhausen sulphuric acid, however, converts it into silicopropionic acid,  $\text{Si}(\text{C}^2\text{H}^5)_2\text{O}^2\text{H}$ , according to the equation:

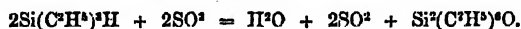


the reaction being analogous to that which tertiary alcohols undergo by oxidation (Butlerow, *Deut. Chem. Ges. Ber.* 1871, 931).

F. *Dehydrating agents*, such as *phosphoric anhydride*, convert triethyl-silicol into its corresponding ether, silicoheptyl oxide,  $\{\text{Si}(\text{C}^2\text{H}^5)_2\}_2\text{O}$ .

Silicoheptyl oxide may also be obtained by the action of hydriodic or sulphuric acid on silicoheptyl-ethyl ether, or by that of potash-ley on silicotriethyl chloride or bromide. It is a colourless, syrupy liquid, boiling at 231°, and of sp. gr. 0.850 at 0°; it is soluble in sulphuric acid, and separates therefrom unchanged on dilution, if heating is avoided; otherwise some triethyl-silicol is formed.

4. *Silicoheptyl hydride*,  $\text{Si}(\text{C}^2\text{H}^5)_3\text{H}$ , is the last product of the action of sodium and zinc-ethyl on silicic ether; it boils at 107°, and resembles the petroleum hydrocarbons in smell; it is insoluble in water and in concentrated sulphuric acid, soluble in ether and alcohol. It is stable in the air, and burns with a brilliant flame, leaving silica; its specific gravity at 0° is 0.751, and its vapour-density 118.4 (calculated 116). Nitric acid and Nordhausen sulphuric acid attack it readily, the latter producing the reaction:



Bromine added drop by drop to the well-cooled liquid, gives hydrogen bromide and silicoheptyl bromide,  $\text{Si}(\text{C}^2\text{H}^5)_3\text{Br}$ , boiling at 161°, and forming silicotriethyl oxide by the action of caustic alkalis; also triethyl-silicol with ammonia.

5. Simultaneously with silicoheptyl hydride, silicon-ethyl,  $\text{Si}(\text{C}^2\text{H}^5)_4$ , is formed by the action of zinc-ethyl and sodium on silicic ether; the body obtained boiled at 151°–153°, and had the properties of the silicon-ethyl of Friedel and Crafts (v. 266).

A small quantity of high-boiling silico-carbonaceous substances was also formed, probably reduction-products of polysilicic ethers.

The specific gravity of the bodies belonging to the silicon-ethyl-oxethyl series diminishes with the diminution in oxygen, but not regularly:

$\text{Si}(\text{C}^2\text{H}^5)_3\text{O}^1$	.	.	.	.	.	.	0.9676
$\text{Si}(\text{C}^2\text{H}^5)_2\text{O}^2$	.	.	.	.	.	.	0.9207
$\text{Si}(\text{C}^2\text{H}^5)_2\text{O}^3$	.	.	.	.	.	.	0.8752
$\text{Si}(\text{C}^2\text{H}^5)_2\text{O}^4$	.	.	.	.	.	.	0.8403
$\text{Si}(\text{C}^2\text{H}^5)_2$	.	.	.	.	.	.	0.8341

The substitution of  $\text{C}^2\text{H}^5$  for Cl raises the boiling point:

$\text{SiCl}^4$	.	.	58°	$\text{SiCl}^3\text{C}^2\text{H}^5\text{O}$	.	104°	$\text{SiCl}^2(\text{C}^2\text{H}^5)_2\text{O}^2$	.	137°
$\text{SiO}^1\text{C}^2\text{H}^5$	.	.	100	$\text{SiCl}^2(\text{C}^2\text{H}^5)_2\text{O}$	.	?	$\text{SiCl}(\text{C}^2\text{H}^5)_3\text{O}^3$	.	151
$\text{SiCl}^3(\text{C}^2\text{H}^5)$	.	.	129	$\text{SiCl}(\text{C}^2\text{H}^5)_3\text{O}$	.	147	$\text{Si}(\text{C}^2\text{H}^5)_4\text{O}^4$	.	155.5
$\text{SiCl}^2(\text{C}^2\text{H}^5)_2$	.	.	143.5	$\text{Si}(\text{C}^2\text{H}^5)_4\text{O}$	.	153			
$\text{Si}(\text{C}^2\text{H}^5)_3$	.	.	152						
$\text{SiCl}(\text{C}^2\text{H}^5)_2\text{O}^2$	.	.	156°	$\text{Si}(\text{C}^2\text{H}^5)_3\text{O}^1$	.	166.5°			
$\text{Si}(\text{C}^2\text{H}^5)_2\text{O}^3$	.	.	159°						

**SILICO-ACETIC ANHYDRIDE**,  $\text{Si}(\text{OC}^2\text{H}^3\text{O})^4$  (Friedel a. Ladenburg, *Ann. Chem. Phys.* [4], xxvii. 428). This compound is obtained by digesting silicon tetrachloride with a mixture of acetic acid and acetic anhydride, and is deposited, on cooling, in beautifully white crystals, apparently belonging to the quadratic system.

Silico-acetic anhydride, when dropped into water, is decomposed with a hissing noise, gelatinous silica and acetic acid being formed. It cannot be distilled under the ordinary pressure, as it is decomposed at a temperature of 160°–170° into silica and acetic anhydride; but if the pressure be reduced to 5 or 6 millimeters, it passes over unchanged at about 148°, and condenses in beautiful white crystalline masses, melting at about 110°. It is decomposed by alcohol, with formation of ethyl acetate and gelatinous silica; cold ether, however, does not change it, although when heated to 80° with that substance, it splits up into silica and acetic anhydride. With dry ammonia it yields acetamide and hydrated silica.

Silico-acetic anhydride is analogous to Ebelmen's silicic ether,  $\text{Si}(\text{OC}^2\text{H}^3)^2$ , and the ethylic silico-acetin,  $\text{Si} \begin{smallmatrix} (\text{OC}^2\text{H}^3)^2 \\ (\text{OC}^2\text{H}^3\text{O}) \end{smallmatrix}$ , obtained by the action of acetic anhydride on silicic ether (v. 264), may be regarded as its triethylic ether.

**SILICOBOROCALCITE.** A mineral named *Winkworthite* by How (*Phil. Mag.* [4], xli. 270), occurring in transparent colourless nodules in the gypsum of Winkworth, Hants Co., Nova Scotia, has been shown by Kenngott (*Jahrb. f. Mineralogie*, 1872, 300) to be a mixture of silicoborocalcite and gypsum. Two analyses by How gave:

	CaO	SO <sup>*</sup>	SiO <sup>*</sup>	B <sup>2</sup> O <sup>3</sup> *	H <sup>2</sup> O
(1.) . . .	31.66	36.10	3.31	10.13	18.80 = 100
(2.) . . .	31.14	31.51	4.98	14.37	18.00 = 100

\* Determined by loss.

The first contains 77.87, the second 67.75 p.c. gypsum.

**SILICODIETHYL ETHER**,  $\text{Si}(\text{C}^2\text{H}^3)^2(\text{OC}^2\text{H}^3)^2$  (p. 1082).

**SILICODIETHYL CHLORETHYLIN**,  $\text{Si}(\text{C}^2\text{H}^3)^2\text{Cl}(\text{OC}^2\text{H}^3)$  (p. 1082).

**SILICODIETHYL CHLORIDE**,  $\text{Si}(\text{C}^2\text{H}^3)^2\text{Cl}^2$  (p. 1082).

**SILICODIETHYL OXIDE** or **SILICON-DIETHYL ESTER**,  $\text{Si}(\text{C}^2\text{H}^3)^2\text{O}$  (p. 1083).

**SILICONEPTYL-ACETIC ETHER**,  $\text{Si}(\text{C}^4\text{H}^7)(\text{OC}^2\text{H}^3\text{O})$  (p. 1083).

**SILICONEPTYL CHLORIDE**,  $\text{Si}(\text{C}^4\text{H}^7)\text{Cl}$  (p. 1083).

**SILICONEPTYL CARBONATE OF SODIUM**,  $\text{Si}(\text{C}^4\text{H}^7)^2\text{CO}^2\text{Na}$  (p. 1083).

**SILICONEPTYL ETHER**,  $\text{Si}(\text{C}^4\text{H}^7)^2(\text{OC}^4\text{H}^7)$  (p. 1083).

**SILICONEPTYL HYDRIDE**,  $\text{Si}(\text{C}^4\text{H}^7)^2\text{H}$  (p. 1084).

**SILICONEPTYL HYDROXIDE**,  $\text{Si}(\text{C}^4\text{H}^7)^2\text{OH}$  (p. 1083).

**SILICONEPTYL OXIDE**,  $\text{Si}^2(\text{C}^4\text{H}^7)^2\text{O}$  (p. 1084).

**SILICON** or **SILICIUM**. On the occurrence and condition of silicon in pig-iron, see pp. 695, 696.

*Occurrence in Plants.*—Ladenburg (*Deut. Chem. Ges. Ber.* v. 569) suggests that at least part of the silica found in plant-ashes may be produced by the combustion of organic compounds in which the carbon has been more or less replaced by silicon. Even the purest cellulose contains a small quantity of silica. The liquid remaining on dialysing the purified alkaline extract of mare's-tail (*Equisetum arvense*) left, on evaporation, pure silica, which, when burnt with copper-oxide, yielded only 1 p.c. carbon dioxide.

*Apparent Volatilisation.*—When the vapour of silicon chloride or fluoride is passed over silicon fused in an atmosphere of hydrogen, compounds are formed which decompose at lower temperatures, and deposit a ring of silicon on the cold part of the tube, as if the silicon had been actually volatilised (Troost a. Hautefeuille, *Compt. rend.* lxxiii. 443; *Chem. Soc. J.* [2], ix. 997; *Jahresb.* 1871, 268).

*Estimation.*—On the estimation of silicon in Cast iron and Steel, see IRON (p. 692). On the estimation of the Fire-resisting qualities of Clays and other Siliceous materials, see CLAY (pp. 353-357).

**SILICON, HALOID COMPOUNDS OF.** *Spectra.*—The haloïd compounds of silicon, heated in a hydrogen flame fed by a jet of air, give band-spectra very similar to one another, and exhibiting a predominance of green. The bands, however, do not appear to be due to pure silicon, since silicon hydride, although very volatile, does not exhibit the same bands, neither are they seen in the electric spectrum of silicon. Silicon fluoride gives only a continuous spectrum, whereas in Geissler's tubes it gives a fine band-spectrum. Silicon bromide gives in such a tube a continuous spectrum with two maxima in the yellow and the indigo, provided the electric tension is weak; with stronger tension the lines of bromine and silicon come out (*Salet, Compt. rend.* lxxiii. 1056).

**Subchlorides and Oxychlorides.** (Troost a. Hautefeuille, *ibid.* lxxiii. 563).—When silicon tetrachloride is passed over fused silicon contained in a porcelain tube, heated nearly to the softening point of porcelain, a liquid is obtained consisting of the tetrachloride mixed with a small quantity of the subchlorides of silicon. The tetrachloride was passed backwards and forwards five or six times over the silicon; and, to prevent decomposition of the subchlorides, a central cooling-tube traversed by a

stream of water at 60° was employed, as in Deville's experiments on dissociation (1st Suppl. 427). To prevent the formation of oxychlorides, air must be carefully excluded from the apparatus.

The tetrachloride boiling at 59° is easily separated from the other chlorides; the latter are separated from one another by repeated fractional distillation.

**Trichloride,  $\text{Si}^2\text{Cl}^4$ .**—Friedel (*Compt. rend.* lxxiii. 1011) prepares this compound by gently heating the tri-iodide with mercuric chloride. It is a colourless and very mobile liquid, having a specific gravity of 1.58 at 0°. It solidifies at  $-1^\circ$  (Friedel); at  $-14^\circ$  (Troost a. Hautefeuille), forming large crystalline plates. It boils at  $146^\circ$ — $148^\circ$ ; the density of its vapour, taken at  $239.4^\circ$ , is 9.7, corresponding with the formula  $\text{Si}^2\text{Cl}^4$ , which requires 9.4.

When strongly heated it gives off a vapour which takes fire spontaneously in the air; heated in closed vessels, it becomes decomposed very slowly at  $350^\circ$  (into tetrachloride and silicon); by heating for twenty-four hours to  $440^\circ$ , about nine-tenths of the chloride employed is decomposed; at  $800^\circ$  the decomposition is complete. Trichloride of silicon is attacked by cold aqueous solution of ammonia, silica and hydrogen being produced. In contact with pure water at zero, it gives a hydrate of the sesquioxide,  $\text{SiO}^2.\text{H}^2\text{O}$ , identical with that obtained by Friedel a. Ladenburg from the tri-iodide (1st Suppl. 1022). This sesquioxide reduces potassium permanganate very rapidly in the cold, and chromic acid very slowly; it has no action, at ordinary temperatures, on solutions of chloride of gold or selenious acid (Troost a. Hautefeuille).

**Dichloride of Silicon,  $\text{Si}^2\text{Cl}^4$ ,** is a liquid which is found mixed with the trichloride, especially when the formation of the latter body is accompanied by that of highly condensed oxychlorides of silicon. Its vapour-density and boiling point have not yet been determined, as it retains pertinaciously small quantities of oxychloride. Decomposed by aqueous ammonia, it evolves a larger proportion of hydrogen than the trichloride. By contact with water at zero, it gives rise to a hydrated oxide, which reduces, not only potassium permanganate and chromic acid, but also solutions of chloride of gold and selenious acid, with separation of metallic gold and red selenium respectively (Troost a. Hautefeuille).

**Oxychlorides.**—Several of these compounds are produced by the action of the induction spark on a mixture of the tetrachloride, the trichlorosilicic oxide,  $\text{Si}^2\text{Cl}^4\text{O}$ , obtained by Friedel a. Ladenburg (1st Suppl. 1021), and oxygen, or better by passing a mixture of oxygen and trichlorosilicic oxide several times through a heated glass tube filled with fragments of porcelain. By fractional distillation of the product the following compounds have been obtained:

Empirical formula	Formula for 2 vols. according to the experimental vapour-density	Boiling point	Vapour-density at $440^\circ$
$\text{Si}^2\text{OCl}^2$	—	—	—
$\text{Si}^2\text{OCl}^4$	$\text{Si}^2\text{O}^2\text{Cl}^4$	136—139°	—
$\text{Si}^4\text{O}^2\text{Cl}^{10}$	$\text{Si}^4\text{O}^2\text{Cl}^{10}$	152—154	—
$\text{Si}^2\text{O}^2\text{Cl}^4$	$\text{Si}^2\text{O}^2\text{Cl}^4$	198—202	15.5
$\text{Si}^4\text{O}^2\text{Cl}^4$	$\text{Si}^4\text{O}^{10}\text{Cl}^{12}$	about 300	21.2
$\text{Si}^4\text{O}^2\text{Cl}^4$	—	above 400	—
$\text{Si}^4\text{O}^2\text{Cl}^4$	—	nearly 40	—

**Tribromide,  $\text{Si}^2\text{Br}^4$ .** This compound is prepared by dissolving the tri-iodide in carbon sulphide, adding bromine in quantity sufficient to displace the iodine, separating the undissolved iodine by filtration, and removing the dissolved iodine by agitation with mercury. The liquid on evaporation yields crystals of the tribromide, which are doubly refractive, and may be distilled without decomposition at about  $240^\circ$ . On treating it with potash, hydrogen is evolved in the proportion of  $\text{H}^2$  to each molecule of  $\text{Si}^2\text{Br}^4$  (Friedel, *Compt. rend.* lxxiii. 1011).

**Chlorobromides.** The *trichlorobromide*,  $\text{SiCl}^3\text{Br}$ , is formed by the action of bromine on silicic chloroform,  $\text{SiCl}^3\text{H}$ . It is a colourless fuming liquid, which boils at  $80^\circ$ , is decomposed by water, and exhibits great similarity to silicon tetrachloride.

The *dichlorodibromide*,  $\text{SiCl}^2\text{Br}^2$ , is also formed by the action of bromine on silicic chloroform, and is found among the products boiling at about  $100^\circ$  (Friedel a. Ladenburg, *Ann. Chim. Phys.* [4], xxvii. 416).

**Chlorosulphhydrate,  $\text{SiCl}^3\text{SH}$ .** This compound, analogous in composition to methylic mercaptan,  $\text{CH}^3\text{SH}$ , was regarded as a sulphochloride by Pierre, who obtained it by passing a mixture of the vapour of silicon tetrachloride and hydrogen sulphide through a red-hot tube (v. 270). It is a colourless liquid boiling at  $66^\circ$ , and having a mixed odour of hydrochloric acid and sulphydric acid, these two acids being formed, together with silica, when it is exposed to the air. When three molecules of alcohol

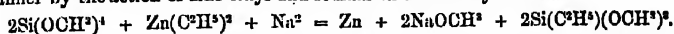
are made to react on one molecule of silicon chlorosulphhydrate, an evolution of hydrochloric acid takes place, and the compound,  $\text{SiSH}(\text{OC}^2\text{H}^5)_2$ , appears to be produced; but if either this compound or the original silicon chlorosulphhydrate be treated with excess of alcohol, a reaction resulting in the formation of silicic ether,  $\text{Si}(\text{C}^2\text{H}_5\text{O})_4$ , takes place. Bromine decomposes silicon chlorosulphhydrate, with formation of the trichlorobromide,  $\text{SiSHCl}^3 + \text{Br}^2 = \text{SiBrCl}^3 + \text{SiBr} + 2\text{HBr}$  (Friedel a. Ladenburg, *loc. cit.*)

**Silicon Subfluoride** is a white, very light powder produced by passing the tetrafluoride over silicon heated nearly to the softening point of porcelain. It is probably a trifluoride, as in contact with water it yields a hydrated oxide which exhibits the same characteristic reactions as that which is formed in like manner from the trichloride (Troost a. Hautefeuille, *Compt. rend.* lxxiii. 563).

**SILICOPROPIONIC ACID**,  $\text{Si}(\text{C}^2\text{H}^5)_3\text{O}^2\text{H}$  or  $\text{CH}^3\text{—CH}^2\text{—SiO}^2\text{H}$  (see **SILICIC ETHERS**, p. 1082).

*Orthosilicopropionic Ethyl-ether*,  $\text{Si}(\text{C}^2\text{H}^5)(\text{OC}^2\text{H}^5)_2$ , formed by the action of zinc-ethyl and sodium on tetramethyl silicate, boils at  $159^\circ$  (p. 1082).

*Orthosilicopropionic Methyl-ether*,  $\text{Si}(\text{C}^2\text{H}^5)(\text{OCH}^3)_2$ , is formed in like manner by the action of zinc-ethyl and sodium on tetramethyl silicate:



The orthosilicopropionic methyl-ether, purified by fractional distillation, boils at  $125^\circ\text{—}126^\circ$ , and has a specific gravity of 0.9747 at  $0^\circ$ . It resembles the corresponding ethyl-compound in odour and appearance, but is more easily decomposed by water, ammonia, &c. Hydriodic acid boiling at  $127^\circ$  acts violently on it, separating a solid body. When left in contact with water it undergoes decomposition, which is accelerated by addition of ammonia. The product of the reaction is a translucent jelly which dries up to a white powder of nearly pure silicopropionic acid (Ladenburg, *Deut. Chem. Ges. Ber.* vi. 1081).

Tetraethyl silicate, zinc-methyl, and sodium do not act on one another at ordinary temperatures. When tetraethyl silicate is heated with zinc-methyl (without sodium) to a temperature above  $300^\circ$ , crystals of the compound  $\text{Zn}(\text{CH}^3)(\text{OC}^2\text{H}^5)_2$  are obtained, and the silicic ether formed at the same time yields by decomposition a combustible silicic acid, probably *silico-acetic acid* (Ladenburg, *loc. cit.*)

**SILICOTETRETHYL**,  $\text{Si}(\text{C}^2\text{H}^5)_4$  (p. 1084).

**SILICOTRIETHYL BROMIDE**,  $\text{Si}(\text{C}^2\text{H}^5)_3\text{Br}$  (p. 1083).

**SILICOTRIETHYL CHLORIDE**,  $\text{Si}(\text{C}^2\text{H}^5)_3\text{Cl}$  (p. 1083).

**SILICOTRIETHYL OXIDE**,  $\text{Si}^2(\text{C}^2\text{H}^5)_6\text{O}$  (p. 1084).

**SILVER.** *Occurrence and Extraction.*—On the occurrence of silver and gold ores in California, and on Rivot's method of working them, see **GOLD** (p. 572).

On Tessié du Mothay's method of extracting silver and gold from arseniosulphides of lead, copper, &c., see p. 573.

On Stetefeldt's furnace for the roasting and chlorination of silver ores, see *Dingl. pol. J.* cxvii. 244.

On Kröncke's method of amalgamating silver ores, see L. Eich (*Chem. Centr.* 1871, 121; *Chem. Soc. J.* [2], ix. 447).

The chemical processes in the amalgamation of gold and silver ores in Washoe are described by A. Hague (*American Chemist*, iii. 98; *Jahresb. f. Chem.* 1872, 951).

Claudet has devised a process for the extraction of silver from copper pyrites. The lyes obtained by treating the pyrites, after roasting and chlorination, with water, usually contain 1 pt. of silver to 10,000 pts. of copper. To separate the silver the solutions of the chloride are mixed with a metallic iodide, best with iodide of potassium; and the deposition of the silver iodide is facilitated by diluting the solution till slimy; and the deposition of the silver iodide is ensured by blowing in steam. The precipitate thus formed contains silver iodide, cuprous chloride, cupric oxychloride, and small quantities of lead and iron. The other salts are removed by dilute hydrochloric acid; the silver iodide is treated with metallic zinc; and the solution of zinc iodide decanted from the reduced silver is used for precipitating the silver from a fresh portion of the crude liquor (*Mechanic's Magazine*, Sept. 1870, p. 207). A favourable report of the results of this process is given by J. A. Phillips (*Chem. News*, xxii. 184).

*Preparation of Pure Silver.*—Grüger (*Dingl. pol. J.* cciii. 111, 292) prepares pure silver from an alloy of silver and copper by heating the solution of the alloy in nitric acid to  $70^\circ$ , and adding calcium carbonate (levigated chalk) as long as effervescence takes place. The whole of the copper is thereby precipitated, while the silver re-

mains in solution together with calcium nitrate. This solution is either precipitated with sodium carbonate, the precipitate ignited and then exhausted with hydrochloric acid, which leaves the silver in the metallic state; or it is digested with silver oxalate, whereby the calcium is separated, and pure silver nitrate remains in solution.

J. Krüger (*ibid.* cxi. 243) prepares pure silver from silver residues, by mixing them with phosphoric ether and repeatedly shaking the mixture. The whole of the silver is then obtained as a black precipitate; and on filtering, washing, and drying, or boiling the still moist precipitate in a porcelain basin with caustic potash, pure metallic silver is left undissolved. To obtain a solid regulus, the dried precipitate is gradually added to potassium carbonate melted in a crucible.

Gladstone & Tribe (*Chem. News*, xxiv. 76) describe the growth of silver crystals during the action of a plate of copper on a solution of silver nitrate.

According to Tribe (*ibid.* xxiv. 135) silver precipitated by copper always contains copper; if, as is generally the case, the solution has absorbed air. If, on the other hand, the air be expelled by carbonic acid, the amount of copper in the precipitated silver is extremely small.

According to C. F. Chandler (*ibid.* xxiv. 10) silver nitrate is immediately reduced to metallic silver by glowing charcoal, the reduced silver penetrating the charcoal and taking the place of the particles of carbon consumed in the reduction, so that it exhibits the exact structure of the original wood.

On Gräber's method of reducing silver from an ammoniacal solution of the chloride with zinc, see *Chem. Soc. J.* [2], ix. 499. On the recovery of silver nitrate from the silver-bath, and from the residues obtained in electroplating, see Gräber, *ibid.* 500.

On the precipitation of silver by ferrous sulphate from the solution of silver sulphate obtained in the 'parting' of gold and silver, see Gützkow (*Deut. Chem. Ges. Ber.* iv. 114; *Chem. Soc. J.* [2], ix. 448).

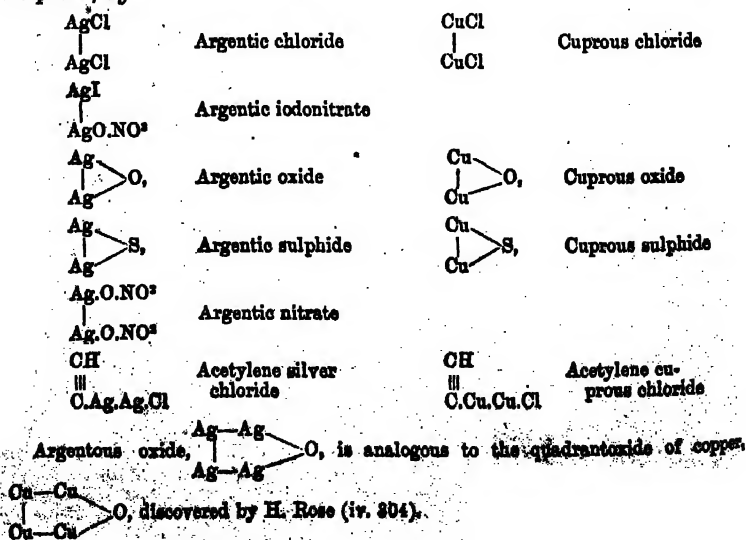
On the alteration undergone by silver vessels, &c., long buried in the earth, see Church (*Chem. Soc. J.* [2], ix. 498) and Schortel (*ibid.* 666).

*Estimation and Separation of Silver.*—On the estimation of silver in presence of mercury, see Debray (*Compt. rend.* lxx. 840, 995; *Jahresh. f. Chem.* 1870, 1014).

On the assaying of silver, see Tookey (*Chem. News*, xxi. 246), Blossom (*ibid.* xxiv. 14, 42, 269), and Busted (*ibid.* xxiv. 243, 259).

On the separation of silver from copper, see COPPER (p. 388).

*Quantivalence of Silver.*—Wislicenus (*Deut. Chem. Ges. Ber.* iv. 63) regards silver (at. w. = 108) as bivalent, on account of the constitution of the argentous salts, of the silver-compounds of acetylene and its homologues, and of the idonitrate of silver,  $\text{Ag}^2\text{INO}^4$  (prepared by prolonged heating of a concentrated solution of silver nitrate in nitric acid with silver iodide, p. 860), and of the corresponding bromonitrate. On this view of the quantivalence of silver, many of its compounds may be represented by formulæ exactly analogous to those of cuprous compounds, with which they are isomorphous; *ej.*





**SILVER, HALOID SALTS OF.** On the refraction and dispersion of light by silver chloride, bromide, and iodide, see *Light* (p. 742).

On the chemical and mechanical changes produced by light in the haloid compounds of silver, see C. Schultz-Sellack (*Deut. Chem. Ges. Ber.* iv. 210, 343; *Chem. Soc. J.* [2], ix. 302, 481).

**Reactions with Mercury Salts.**—Preuss observed that silver iodide dissolves abundantly in a solution of mercuric nitrate, the solution solidifying on cooling to a crystalline mass consisting of a double compound of silver iodide and mercuric nitrate,  $4\text{AgI} \cdot 2\text{HgN}^2\text{O}^6 + \text{H}_2\text{O}$  (*Gmelin's Handbook*, vi. 199). Afterwards Wackenroder (*ibid.* 159, 165) observed that the bromide and chloride of silver likewise dissolve readily in aqueous mercuric nitrate; and Liebig found that a warm solution of silver chloride in mercuric nitrate deposits, on addition of water and cooling, shining crystals of silver chloride (*Ann. Ch. Pharm.* lxxi. 128). These statements have been confirmed in their essential particulars by Debray (*Compt. rend.* lxx. 995), who further states that iodide and bromide of silver crystallise, on cooling, from a hot solution of mercuric nitrate. He also confirms the statement of Risse (iv. 104) that silver chloride dissolves in aqueous silver nitrate, but he was not able to obtain the definite compound of the two mentioned by Risse, the crystals which separated from the hot saturated solution consisting simply of silver chloride.

**Chloride, AgCl.** According to Stas (*Compt. rend.* lxxiii. 998), this compound exists in four different states: 1. gelatinous; 2. curdy-flocculent; 3. pulverulent; 4. granulo-sealy-crystalline, as obtained by fusion. In the last-mentioned state, its solubility in water at ordinary temperatures = 0, or at least does not attain the limit at which dissolved silver chloride can still be recognised, a limit which Stas fixes at 1 part in ten million. Its solubility in boiling water is proportionally great, but diminishes rapidly as the temperature falls, and is equal to nothing at  $16^\circ$ . The curdy modification obtained by precipitation from cold dilute solutions is the most soluble, but its solubility diminishes as the flocks spontaneously condense, or when the precipitate is rendered pulverulent by agitation. A solution of flocculent or pulverulent silver chloride in pure water, or water acidulated with nitric acid, is precipitated both by silver nitrate and by hydrochloric acid. To precipitate a unit of silver or of chlorine in the state of dissolved flocculent or pulverulent silver chloride requires 3 units of chlorine, or of silver (as nitrate). The precipitation is always complete. The salts formed in the reaction simultaneously with the silver chloride have no influence on the solubility of the chloride in pure or acidulated water. The presence of nitric acid does not increase the solubility of curdy or flocculent silver chloride, whereas that of the pulverulent variety increases in proportion to the quantity of nitric acid contained in the water. Saturated solutions of granular silver chloride are likewise precipitated both by chlorine and by silver nitrate, and the precipitation of a unit of silver or of chlorine, as silver chloride, likewise requires 3 units of chlorine or of silver, but the separation of the dissolved granular silver chloride is never complete.

With hydrobromic or hydriodic acid the precipitation may always be so conducted that the liquid shall not give a precipitate either with silver nitrate or with a haloid salt.

Pierre (*Compt. rend.* lxxiii. 1090) observes that when solution of silver nitrate is added drop by drop to concentrated hydrochloric acid, the precipitate formed disappears so rapidly that it sometimes escapes observation altogether. The weight of the silver chloride dissolved may exceed one-half p.c. of the weight of the hydrochloric acid employed. The subsequent addition of water very slowly reprecipitates the whole of the chloride.

When nitric acid is distilled over a small quantity of silver chloride, in the state of powder, the latter disappears gradually; this is, however, not a simple solution, because, at the end of the operation, crystallised silver nitrate is found in the retort instead of the chloride.

Thorpe (*Chem. Soc. J.* [2], x. 453) finds that 100,000 pts. of strong nitric acid dissolve about 2 pts. of pure, white silver chloride, and that the solubility is not sensibly affected by the presence of lower oxides of nitrogen in the acid, but that as the chloride darkens by exposure to light, less of it is taken up by the acid, 100,000 pts. of the acid dissolving only 0.8 pt. of the blackened silver chloride.

**Fluoride, AgF.** The following observations on this compound have been made by Gore (*Proc. Roy. Soc.* xx. 70), in addition to those reported in the 1st *Suppl.* (p. 1027).

The action of iodine and heat on silver fluoride produces iodine fluoride (a volatile, colourless, fuming liquid) and silver iodide, also, if the temperature approaches redness, corroding the platinum vessels and forming a double salt of silver iodide and platinum fluoride.

Silver fluoride is reduced by heating in dry *cyanogen vapour*, or *hydrogen cyanide*, or *coal gas*, but is unaffected by carbon oxide or dioxide, silicon fluoride, sulphur dioxide, or sulphur fluoride vapour, or by liquid cyanogen, carbon bisulphide, hydrocyanic acid (anhydrous), carbon tetra- or trichloride, pure carbon, or boron crystals. Fused in the vapour of *carbon tri- or tetrachloride*, it forms silver chloride, as well as an insoluble double salt of silver and platinum by corrosion of the vessels. A solution of bromine or iodine in carbon tetrachloride or bisulphide is quickly decolorised by agitation with silver fluoride. The fluoride is also decomposed violently by fusion with vitreous boric acid, silicon, dry silica, or sulphur. In the latter case sulphur fluoride, a heavy colourless gas of a peculiar dusty odour, is evolved. *Sulphur chloride* with silver fluoride, either fused or in solution, gives silver chloride and vapour of sulphide. *Carbon bisulphide* at a red heat yields silver sulphide and carbon tetrafluoride,  $4\text{AgF} + \text{CS}_2 = \text{CF}_4 + 2\text{Ag}_2\text{S}$ .

Carbon tetrafluoride is also said to be formed when silver fluoride is added to liquid carbon bisulphide containing bromine or iodine in solution.

**Iodide.** AgI. According to A. Vogel (*N. Rep. Pharm.* xx. 120), silver iodide is not decomposed by boiling aqueous potash, the grey colour which it acquires being due to molecular alteration; native silver iodide from Mexico exhibits a similar colour. Even by fusing silver iodide with potassium iodide, only a very incomplete decomposition is effected, and the separation of metallic silver from it by zinc and hydrochloric acid is less complete than in the case of the chloride. When dry silver chloride is triturated with pulverised iodine, and the excess of iodine removed after some time by solution in alcohol, the chloride of silver is found to be partly converted into iodide, and no longer dissolves completely in ammonia. Silver iodide is partly decomposed by a strong heat, with evolution of iodine. In closed vessels it volatilises at a white heat.

On the compounds of silver iodide with silver nitrate, see NITRATES (p. 860).

**SILVER OXIDES.** To decide whether the alkaline reaction of silver oxide is due to adhering alkali, or belongs to the oxide itself, A. Vogel (*N. Rep. Pharm.* xx. 93) precipitated an acid solution of silver nitrate with lime-water, keeping the silver nitrate in excess, and washed the precipitated silver oxide thoroughly with hot water. The still moist oxide, laid upon reddened litmus paper, immediately produced a distinct blue spot, and on recently prepared turmeric paper a brown spot. Silver nitrate also, especially after fusion, has, according to Vogel, an alkaline reaction. Crystals of silver nitrate lose their acid reaction and become alkaline when their solution is boiled with silver foil or silver oxide.

*Peroxide*,  $\text{Ag}_2\text{O}^2$ .—For the preparation of this oxide, Böttger (*Zeitschr. f. Chem.* [2], vi. 82) recommends the electrolytic method employed by Ritter (v. 303). The peroxide sets fire to hydrogen sulphide and oil of cloves, and eliminates nitrogen from aqueous ammonia, as formerly observed by Grothuss (*Jahresb.* 1852, 423). When it is triturated with gold sulphide, the mixture quickly takes fire.

**SILVER SULPHIDES.** A double sulphide of silver and iron, called *silver pyrites*, occurring with proustite in the mineral veins of Joachimsthal, forms, according to S. von Waltershausen (*Jahrbuch. f. Min.* 1868, 725), very small monoclinic crystals of hexagonal character. Colour, light lead-grey with a tinge of yellow; streak black; brittle; fracture uneven; hardness = 3·5; sp. gr. = 6·47. An analysis made with a very small quantity of material gave 39·3 p.c. Fe, 26·6 Ag, and 34·2 S, agreeing with the formula  $\text{Ag}_3\text{S}_3\text{FeS}_2$ . According to Tschermak, however (*ibid.* 726), silver pyrites is not a distinct mineral species, but a pseudomorph (consisting of marcasite, pyrrhotin, argentite, and pyrrargyrite), and probably identical with Zippe's pseudomorph of iron pyrites after pyrrargyrite and stephanite. On the other hand, A. Schrauf (*ibid.* 1872, 94) maintains that the mineral is not a pseudomorph, but a distinct species, crystallising in the rhombic system, and isomorphous with stannbergite. He found the specific gravity to be 6·53 at 13°, and the amount of silver 21·2 and 22·3 p.c. the above formula requiring 24·77 p.c.

On the *sulphide of silver and gold*,  $5\text{Ag}_2\text{S} \cdot 2\text{Au}_2\text{S}_3$ , discovered by Muir, see GOLD (p. 576).

**SINKOWITE.** *Blodite*.—A sodio-magnesian sulphate,  $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 + 4\text{H}_2\text{O}$ , occurring in the carnallite of Stassfurt (*Jahresb. f. Chem.* 1871, 1181; 1872, 1141).

**SINALBIN**,  $\text{C}^8\text{H}^4\text{N}^2\text{S}^2\text{O}^{14}$ . A constituent of the seed of white mustard. See MUSTARD (p. 832).

**SINKOWITE.** Syn. with POTASSIUM MYRONATE (iii. 1079).

**SNARUMITE.** This name is given by Breithaupt (*Jahrb. f. Min.* 1872, 330).

to a mineral from Snarum in Norway, agreeing in composition with spodumene, but differing from it (being micaceous) in physical properties:

$\text{SiO}^2$	$\text{Al}^2\text{O}^2$	$\text{Fe}^2\text{O}^2$	$\text{Mn}^2\text{O}^2$	$\text{CaO}$	$\text{Na}^2\text{O}$	$\text{Li}^2\text{O}$	Loss by ignition
67.42	28.21	0.42	0.18	0.24	09.3	2.15	0.23 = 99.78.

**SODA.** On the composition of Crude Soda, and the loss of Sodium in Leblanc's process, see Scheurer-Kestner (*Compt. rend.* lxx. 1352; *Jahresb. f. Chem.* 1870, 114); also Maclear (*Chem. News*, xxv. 54; *Jahresb.* 1872, 975).

On the quantity of Arsenic introduced into the products of the soda-manufacture from the pyrites used for the preparation of sulphuric acid, see H. A. Smith (*Chem. News*, xxiii. 221; *Jahresb.* 1871, 1014).

On the recovery of Sulphur from Soda-waste, see L. Mond (*Dingl. pol. J.* ccii. 266; *Jahresb.* 1871, 1015), Stahlsehmidt (*Dingl. cv. 229*; *Jahresb.* 1872, 977).

Bachet's process for preparing caustic soda by decomposing common salt with litharge and lime is described by R. C. Clapham (*Chem. News*, xxi. 148; *Jahresb.* 1870, 1114); further by Clapham & Ball (*American Chemist*, iii. 181; *Jahresb.* 1872, 978).

A method of preparing *silicate of soda* by decomposing common salt with silica and aqueous vapour is given by A. Ungerer (*Dingl. pol. J.* cxvii. 343; *Jahresb.* 1870, 1116).

**SODIUM.** On the solubility of sodium in liquid ammonia, see p. 60.

**Bromide, NaBr.**—Castelholz (*Compt. rend.* lxx. 1050) prepares this salt by decomposing ammonium bromide with an equivalent quantity of pure hydrate or carbonate of sodium. The ammonium bromide is prepared by dropping bromine into pure dilute ammonia, and purified from the much more soluble iodide by recrystallisation.

**Chloride, NaCl.**—On the crystallisation of this salt in transparent cubes from solutions containing ferric chloride, magnesium chloride, &c., see Buchner (*N. Rep. Pharm.* xx. 151; *Jahresb.* 1871, 274; *Chem. Soc. J.* [2] ix. 311).

**Hydrate, NaHO.**—O. Hermes (*Pogg. Ann.* cxix. 170; *Deut. Chem. Ges. Ber.* iii. 122) observed that a solution of caustic soda, of sp. gr. 1.365, deposits the hydrate at low temperatures in crystals having the composition  $2\text{NaHO} \cdot 7\text{H}^2\text{O}$ . These crystals were described in 1863 by G. Roso, who regarded them as monoclinic. According to Hermes, however, they are rhombic prisms of  $98^\circ$  slightly truncated on the acute lateral edges. They are transparent and colourless, with a vitreous lustre, melt at  $6^\circ$ , and separate tolerably pure from a solution of caustic soda containing chloride, sulphate, and carbonate of sodium.

**SOLFATARAS.** On the gases evolved from the solfataras of Vesuvius and the Campi Flegrei, see GASES (p. 560).

**SORBIC ACID,  $\text{C}^6\text{H}^6\text{O}^2$ .** This acid, which Hofmann obtained from unripe mountain-ash berries (v. 352), has been further examined by Barringer & Fittig (*Zeitsch. f. Chem.* 1870, 425; *Ann. Ch. Pharm.* clxi. 307) with the view of determining whether it is analogous in its chemical relations to the acids of the series  $\text{C}^6\text{H}^{2n-4}\text{O}^2$ , whether it is analogous in its chemical relations to the acids of the series  $\text{C}^6\text{H}^{2n-2}\text{COOH}$  (palmitic, stearic, lichenolic). These chemists confirm Hofmann's statements with regard to the properties of sorbic acid, excepting as to its alleged capability of volatilising without decomposition. They find indeed that the pure acid begins to boil at  $225^\circ$ , part of it distilling unaltered at this temperature, while the rest is converted, with emission of a distinct odour of acrolein, into a very thick brown mass, hardening on cooling to a resin, from which sorbic acid is not regenerated by boiling with water.

When 1 mol. sorbic acid is triturated under water with 2 mols. bromine, a semifluid mass is obtained, consisting of the solid tetrabromide of sorbic acid,  $\text{C}^6\text{H}^2\text{Br}^4\text{O}^2$ ; isomeric or identical with tetrabromocaproic acid, and a liquid which is probably the dibromide  $\text{C}^6\text{H}^4\text{Br}^2\text{O}^2$ . On dissolving the crude product in hot alcohol, and leaving the solution to cool, or allowing the alcoholic solution to evaporate spontaneously, a thick oil is obtained which, when separated from the mother-liquor, solidifies, for the greater part, in a few days. By pressing the product, dissolving it, and repeating these operations several times, the tetrabromide is finally obtained in large well-defined, apparently monoclinic crystals, which are transparent, have a vitreous lustre, and no longer separate from hot alcohol in the liquid state. This compound is very sparingly soluble in water even at the boiling heat, and crystallises therefrom in capillary needles. It melts at  $178^\circ$ – $179^\circ$ , dissolves in alkaline carbonates, and is precipitated therefrom by acids without alteration.

**Hydrosorbic Acid,  $\text{C}^6\text{H}^6\text{O}^2$ .** This acid, belonging to the oleic series, and isomeric with pyrotaradic and ethyl-crotonic acid, is easily formed by treating sorbic acid with water and sodium-amalgam. It is a colourless liquid having a peculiar

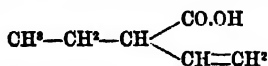
odour of perspiration and slightly soluble in water. Sp. gr. = 0.969 at 10°. Boiling point 201° (204°-205° corr.) Remains liquid at -18°.

**Calcium Hydrosorbate**,  $(C^4H^4O^2)^2Ca + H^2O$ , crystallises easily in groups of small, very soluble needles. The **barium salt**,  $(C^4H^4O^2)^2Ba$ , crystallises in very beautiful anhydrous needles having a silky lustre, easily soluble in water. The **copper salt**,  $(C^4H^4O^2)^2Cu$ , is a greenish-blue precipitate which loses part of its acid at 100°, and melts to a deep green liquid at 180°-185°. The **silver salt**,  $C^4H^4O^2Ag$ , is a white precipitate insoluble in water, turning brown at 90°-100°. The **ethyl ether**,  $C^4H^4O^2C^2H^5$ , is a colourless liquid, having a fruity odour, boiling at 166°-167°; slightly soluble in water.

**Bromine** acts violently on hydrosorbic acid at ordinary temperatures, with evolution of hydrogen bromide, but at low temperatures the additive compound,  $C^4H^4O^2Br^2O^2$ , hydrosorbic dibromide or dibromo-caproic acid, is formed. It is a colourless viscid liquid insoluble in water, reconverted by alcoholic potash into sorbic acid.

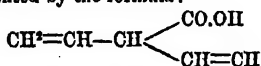
Hydrosorbic acid is not altered by heating it with *potassium hydrate* to 180°; but if the heat be raised till gas begins to be evolved, carbonic and butyric acid are formed, but no other acid of the fatty series.

**Constitution of Hydrosorbic and Sorbic acids**.—Fittig and Barringer represent hydrosorbic acid by the formula :

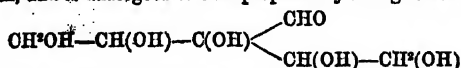


which accords best with its behaviour with fused potash, whereby the group  $\text{CH}=\text{CH}^2$  is split off and replaced by hydrogen, producing butyric acid,  $\text{CH}^2-\text{CH}^2-\text{CH}^2-\text{COOH}$ , while the group  $\text{CH}-\text{CH}^2$  itself is oxidised to oxalic and finally to carbonic acid.

Sorbic acid may be represented by the formula :

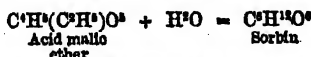


which explains its probable resolution by distillation into two molecules of acrolein,  $\text{CH}^2=\text{CH}-\text{COH}$ , and is analogous to that proposed by Fittig for sorbin, viz. :



Barringer and Fittig doubt the existence of Hofmann's *parasorbic acid*, and conclude from their experiments that it was nothing but impure sorbic acid. Hofmann describes it as a liquid having less decided acid properties than sorbic acid, and dissolving in alkaline carbonates without evolution of carbonic acid. Barringer and Fittig, however, find that it dissolves in warm sodium carbonate with violent evolution of carbonic acid, and that the filtered solution, concentrated and mixed with hydrochloric acid, yields pure crystalline sorbic acid.

**SORBIN**,  $C^4H^{10}O^4$ .—A sugar, isomeric with glucose, obtained from the fermented juice of mountain-ash berries (v. 352).<sup>\*</sup> Pelouze, who discovered it, was unable to decide whether it existed ready formed in the fruit, or was a product of decomposition. Byschl (*Jahresh. f. Chem.* 1854, 664) found no sorbin in the juices of ripe mountain-ash berries; and Delffs (*Chem. News*, xxiv. 75; *Jahresh.* 1871, 799) has observed that no sorbin is obtained when an attempt is made to combine the preparation of malic acid from the berries with that of sorbin, the malic acid being for that purpose precipitated by lead acetate before the preparation of sorbin by Pelouze's process is commenced. When the latter process is strictly followed, a large quantity of sorbin crystals is obtained, but no malic acid is found in the fermented juice. Delffs therefore supposes that there is an intimate connection between the disappearance of the malic acid and the formation of sorbin, which may perhaps be represented by the equation :



At all events, sorbin does not exist ready formed in the berries of the mountain-ash.

Sorbin, treated with *bromine* and water, is oxidised to glycollic acid (Hlasiwetz and Habermann, *Ann. Ch. Pharm.* clv. 120).

**SORBITE**,  $C^4H^{10}O^6$  (Boussingault, *Compt. rend.* lxxiv. 939). A non-fermentable sugar, isomeric with mannite and dulcete, obtained from the juice of mountain-ash

<sup>\*</sup> There called *sorbin*; but this latter name is now applied to a sugar isomeric with mannite, likewise obtained from mountain-ash berries (see the next article).

berries. It may be separated from the fermented juice, but is not a product of fermentation, since it may also be obtained from the fresh juice immediately after expression.

Sorbitol is nearly insoluble in cold alcohol, moderately soluble in boiling alcohol, from which it separates on cooling in translucent, opalescent, warty masses. From aqueous solution it is obtained in nacreous crystals which have the composition  $2C^6H^{14}O^6.H^2O$ , and give off their water of crystallisation when heated above  $100^\circ$ . It differs from mannitol and dulcitol by several properties. It melts in the hydrated state at  $102^\circ$ , in the anhydrous state at  $110^\circ$ – $111^\circ$ , whereas mannitol melts at  $165^\circ$  and dulcitol at  $182^\circ$ . With water it forms a syrupy solution which, after some time, deposits crystals, whereas an aqueous solution of mannitol has no syrupy consistence. The crystals of sorbitol are so thin that their form is difficult to determine, whereas mannitol forms quadratic prisms, and dulcitol oblique rhombic prisms (sorbitol also forms well-defined crystals, v. 352, 353). It is inactive to polarised light, and does not reduce an alkaline cupric solution. Sulphuric acid does not carbonise it, even with the aid of heat, but dissolves it, the solution neutralised with barium carbonate yielding insoluble barium salts.

**SPECTRAL ANALYSIS.** There appears to be little doubt that differences in the molecular structure, as in the case of allotropic modifications of the elements, and also in the case of compound bodies, are accompanied by distinct differences in the spectra of these substances. From a theoretical point of view this would appear likely, as the vibrations taken up or given out by a complicated system of molecules must be different from those absorbed or emitted by a simpler system. The peculiar differences between the spectra of elementary bodies and of compounds has already (1st Suppl. 1031) been pointed out. The characteristic of the compound-spectrum, as seen at temperatures below the point of dissociation, is that it consists of bands or maxima of light, each containing rays of more than one degree of refrangibility; whilst that of the elementary-spectrum is the existence of fine lines, each of which, as a rule, contains light of one degree of refrangibility only. These definitions, however, do not hold good universally; thus in the spectra of many metals, such as Al, Pb, Mn, Cd, Sn, Zn, Sb, and Ba (Lockyer, *Phil. Trans.* 1873, Part I. plates 11, 12), broad bands occur which are especially seen as lines winged at the poles, and the absorption-spectra of certain compounds, as those of the higher oxides of nitrogen, are chiefly made up of masses of the finest lines and are not banded.

It may, however, be admitted (with Lockyer, *Proc. Roy. Soc.* June 11, 1874) that the first stage of molecular complexity corresponds with the line-spectrum; that the second stage is represented by the channelled-space-spectrum; and that the third stage corresponds with a continuous spectrum (whether emissive or absorptive). Lockyer (*loc. cit.*) proposes to extend the comparison still further, as he interpolates two other stages after that of the channelled spaces—(a) in which the general absorption begins at the blue end and does not extend into the least refrangible rays, (b) in which the general absorption begins in the red, not reaching to the blue. The three divisions as above given appear, however, to be as many as can safely be relied upon, and we should do well to remember Kirchhoff's caution respecting change of the spectra with change of luminosity (1st Suppl. 1032).

As a rule, too, it may be admitted that the spectra of compounds contain more bands than those of the elements, but no sharp distinction can be drawn even here. Thus, for instance, certain lines, as those of sodium and hydrogen, widen under certain conditions; and that this widening cannot be explained by the supposition that the gas is becoming of a more complicated molecular structure, is shown by the fact that these bands make their appearance at a temperature higher than that at which the lines are frequently seen; thus when the Leyden jar is interposed in the circuit of a Geissler's tube containing hydrogen, the lines are widened, and here it is evident the temperature cannot be lower than when the narrow lines were seen without the jar.

As regards the existence of more than one spectrum for any given elementary body, we have in the case of sulphur two spectra; a continuous one to begin with, which breaks up on heating into a second spectrum of channelled spaces. In the case of oxygen we should expect that the absorption-spectrum of the denser ozone would exhibit a difference from that of ordinary oxygen, but observations on this point have hitherto not been made. The spectrum of nitrogen has recently been much worked upon, without, however, completely solving the question of its dual spectrum (*ibid.* i. 1031). When the spectrum of nitrogen containing a trace of air or oxygen is examined in a vacuum-tube, the characteristic channelled spaces usually called the nitrogen bands are invariably seen. If now the gaseous contents of the tube be freed from oxygen and vapour of water by heating some metallic potassium or sodium in the tube, these bands never again appear (Schuster, Stearn, Willner). The lines which make their appearance after the sodium has been heated in the gas seem to vary with the mode in which the experiment is conducted; thus Willner obtained the carbonic-acid-spectrum

(perhaps from the grease of his glass stopcocks); Stearn saw the acetylene-spectrum (probably because he used sodium which had been in contact with rock-oil); and Schuster saw only the hydrogen lines (his sodium never having been in contact with oil). The fact that the lines of hydrogen appear, whilst no nitrogen lines are seen, is certainly very remarkable, and cannot be easily explained; for a mixture of air and hydrogen always gives the air- as well as the hydrogen-spectrum. Thus ammonia gas collected with great care, and decomposed by the spark, always shows the air-band together with the hydrogen lines. It is possible that the nitrogen lines are not seen by reason of the bad conductivity of the gas, and the most probable supposition (in spite of the experiments and conclusions of Willner and Salet) appears to be that the ordinary band-spectrum of nitrogen is that of an oxide. At any rate, if this is due to nitrogen itself, this substance must exist in three allotropic modifications, for the band-spectrum consists of two different spectra, the red bands and the blue bands. These two spectra can readily be separated so that one tube shows only the red and another only the blue bands, the former corresponding with a higher temperature than the latter. As regards hydrogen there can be no doubt that Angström's opinion (*ibid.* 1032) is correct, and that only one spectrum of hydrogen is known.

Goldstein (*Phil. Mag.* [4], 49, p. 333) has recently come to the conclusion, in opposition to Willner's views, that the change from a band- to a line-spectrum in the case of gaseous spectra is to be ascribed rather to a change of temperature than to a change of density in the gas.

**Absorption-Spectra of the Metals.**—New absorption-spectra of the metals sodium and potassium have recently been observed by Roscoe and Schuster (*Proc. Roy. Soc.*, June 11, 1874), who examined the absorption of the vapours of these metals at low temperatures, first heated in glass—and afterwards in iron tubes. These new spectra are of a complicated character, consisting of several splendid series of channelled spaces both in the red and blue portions of the spectrum; that these are caused by the vapour of the metals in question, and not by any oxide, is proved by the facts that the metal contained in the sealed glass tubes was frequently melted and allowed to stand until the surface remained perfectly bright and metallic, showing absence of every trace of oxygen; also that when the metals were heated in an iron tube filled with hydrogen the peculiar bands disappeared at once when air was admitted. The following numbers give the wave-lengths of the chief bands of these two spectra in tenth-metres.

Bands of potassium shaded off towards red:—

6844	6450	6311	5949	5763
6762	6430	6300	5930	5745
6710	6400	6275	5901	5732
6666	6370	6059	5860	5712
6615	6357	6033	5842	5700
6672	6350	6012	5821	5690
6534	6331	5988	5802	5674
6494	6322	5964	5781	5667

Absorption bands of sodium, wave-lengths in tenth-metres:—

5668	6361	6105	5999	4964
5616	6272	6092	5150	4927
5552	6235	6071	5120	4880
5499	6192	6051	5082	4863
5450	6162	6035	5038	4832
5405	6149	6016	5002	4810

From this we see that each of the alkaline metals exhibits two distinct absorption-spectra, one consisting of channelled spaces and one of dark lines coincident with the ordinary emission-spectrum of the metal.

Lockyer & Roberts (*Proc. Roy. Soc.* xxiii. 354) have obtained absorption-spectra of several heavy metals by volatilizing them in a lime crucible heated by the oxygen-hydrogen flame, and they thus found that, in addition to the well-known spectra, channelled-space-spectra are produced by the vapours of certain metals, and such spectra are produced by vapours which are competent to give, at other times, not only line-spectra, but continuous spectra in the blue or blue and red.

**Metallic Spectra.**—A most remarkable feature in the spectra of metals has been pointed out by Lockyer (*Phil. Trans.* 1873, 233), viz. that when the electric-spark-spectrum of any metal—say of iron—is examined by throwing an image of the electrodes on to the slit of the spectroscope, a difference in length of the several metallic lines is observed; and in this way, that the brightest of the metal lines is invariably the longest. In other words, the vapours close to the electrodes

give lines which disappear at a greater distance from the electrode, causing the appearance of long and short lines in the spectrum. The length of the lines appears to depend on the pressure to which the vapour is subjected; thus the lines gradually disappear when the pressure is reduced (the electrodes being inclosed in glass tubes), the shorter lines disappearing first and the longest lines remaining longest visible. When the metals are combined with a metalloid (chlorine, for instance) the spark-spectrum of the compound exhibits only the longest and brightest of the metal lines, all the shorter lines (as is the case under diminished pressure with the metal alone) having disappeared. The proportion of the metal lines seen in the spark-spectrum of the compound appears to be connected with the atomic weight (or, more probably, with the volatility) of the metal; thus 60 p.c. of the lines of lithium are seen in the spectrum of the chloride of lithium, whereas 8 p.c. of the barium, and only 3 p.c. of the lead, lines are seen under like conditions (Lockyer).

A valuable contribution to our knowledge of metallic spectra has recently been made by Thalen (*Kongl. Svenska. Vet. Akad. Handl.* Bd. 13, No. 4, 1874), in his accurate maps of the spectra of Yttrium, Erbium, Didymium, and Lanthanum.

*Applications to Solar Chemistry.*—Lockyer applies these observations to elucidate the peculiarities of the solar spectrum. It is well known that all the lines of the metallic elements in the solar atmosphere are not reversed, but without exception those lines which are found to be reversed are the *longest lines*. Applying this discovery Lockyer has added the following metals to the last list of solar elements given by Thalen: 1. (*Proc. Roy. Soc.* Dec. 12, 1872) zinc (rejected by Thalen from Kirchhoff's first list); 2. (*ibid.*) aluminium (rejected both by Kirchhoff and Thalen); 3. (*ibid.* Nov. 27, 1873) strontium; 4. cadmium; 5. lead; 6. cerium; 7. uranium.

*Map of the Solar Spectrum.*—Lockyer is engaged (*Proc. Roy. Soc.* xxiii. 152) in mapping the portion of the solar spectrum, together with the spectra of the metals, extending from w. l. 3900 to 4100, on a much larger scale than has hitherto been attempted, viz. nearly four times that of Angström's 'spectre normal.' This has been done by the aid of photography, and the spectra of the following elements have been photographed side by side with the solar spectrum, and the coincidences shown: Fe, Co, Ni, Mn, Ca, U, Cr, Ba, Sr, Ca, K, Al. The advantages of the photographic method over eye-observation may be estimated from the following comparisons of the number of lines obtained in the above region by different observers:

Number of lines in Angström's 'Spectre normal'	39
" " " and Thalen's map	185
" " Cornu's map	205
" " the New map	518

It will serve further to illustrate the advantages of this method if we compare the number of lines in the spectra of metals already observed with the number of lines of the same metal as given by Angström in his 'spectre normal':

*Region 3900 to 4100.*

Metal	New map	Angström's map and Thalen's
Fe	71	19
Mn	53	12
Co	47	—
Ni	17	—
Ce	163	—
U	18	—
Cr	24	—
Ba	7	—
Sr	5	—
Ca	7	6
K	2	—
Al	2	2
Total	416	39

*Spectra of Chemical Compounds.*—Lockyer (*ibid.* 1873, 285) has investigated the number and position of the true metallic lines seen when the electric spark is allowed to pass from various compounds of the given metal. The following lead salts were examined— $\text{PbF}_2$ ,  $\text{PbCl}_2$ ,  $\text{PbBr}_2$ ,  $\text{PbI}_2$ ; and it appears that the decrease in length and number of the metal lines observed in the case of the above salts follows the increase in the atomic weight of the non-metallic element, the lines dying out in the order of

their length. In other words, the greater the number of metallic lines which appear, the greater is the amount of dissociation going on. This was also found to hold good with the haloid compounds of the metals of the alkalis and alkaline earths.

*Spectra of Mechanical Mixtures of Metals.*—When an alloy of two or more metals is used as electrode, only certain of the lines of each metal are seen, and Lockyer (*loc. cit.*) has shown that the lines of the metal present in smallest quantity appear in least number, the shortest lines disappearing first as the percentage of metal is reduced, so that at last only one or two lines, and these the longest lines, remain.

*Suggestions for a possible quantitative Spectrum Analysis.*—By making use of the observations mentioned in the last paragraph the foundation of a quantitative-spectrum test is rendered possible (Lockyer, *Phil. Trans.* 1873, 261; 1873, 655; and 1874, 481; Lockyer & Roberts, *Proc. Roy. Soc.* 1873, 507). A series of experiments made with the gold-copper alloy used in coinage showed that it is possible, by carefully adjusting the striking distance of the spark, and by accurately observing the differences of length and breadth of certain lines seen in the spectrum of the alloy, to distinguish by spectrum observations differences in the composition of the alloy even smaller than those ascertainable by the ordinary assay. Thus, in the above alloy,  $\frac{1000}{10000}$  increase in the gold made the lines shorter, and a similar increase in the copper made them longer.

Should it prove possible to ensure accuracy of observation and uniformity of condition, the practical importance of this branch of the inquiry can scarcely be overrated.

*Photographing Spectra.*—No process of mapping or drawing spectra of any kind can compete in accuracy and delicacy with photography. The photographs of the solar spectrum obtained, first by Rutherford and more recently by Draper (*Phil. Mag.* [4], xvi. 419), are models of accurate experimentation. Lockyer has applied this process to the delineation of the spark of the electric-arc-spectrum (*Phil. Trans.* 1874, 484, Bakerian lecture), a camera carrying a  $5 \times 5$ -inch plate and a 3-inch lens of 23-in. focus replacing the observing telescope of the spectroscopic. The beam passing through the collimator and prisms was very small; the electric lamp was placed on its side so that the arc was horizontal, and thus the image of the short lines was projected on to the middle of the field, the longer ones extending beyond them on either side. The solar spectrum was used as a scale, an image of it being allowed to fall immediately adjacent to the metallic spectrum under examination. For this purpose a portion of the slit was covered up whilst the solar-spectrum passed through the free part. This portion was then closed by a shutter, and another portion opened for the metal-spectrum. In this way several metallic spectra may be photographed on a single plate, and the solar spectrum may be added for comparison. Of course maps of only those portions of the spectrum can thus be obtained in which the rays are capable of acting on the sensitive film; but, on the other hand, this method is capable of giving us information concerning the existence of lines in the ultra-violet portion of the spectrum which are invisible to the eye. Lockyer (*ibid.* 1874, 805) has constructed maps of the spectra of calcium, barium, and strontium from photographs taken by the method above described. The maps comprise the portion of the spectrum extending from wave-length 3900 to wave-length 4509.

*On Lines coincident in different Spectra.*—Lockyer (*loc. cit.* 511) has come to the conclusion that many of the cases hitherto supposed to be coincidences of lines in the spectra of two metals are due to the presence of traces of the one metal in the other. He bases his conclusions on the fact that most of these so-called coincidences, such as line 4607.5 of strontium, are found to be long in the spectrum of one metal and short in that of the other. Thus the above line is long in strontium, appears in calcium as a short line, and the coincidence is due, according to Lockyer, to the presence of a trace of strontium in the calcium. This is as a rule true in the case of those lines of iron, cobalt, chromium, and manganese, coincident with lines of calcium, which in the calcium-spectrum are long, but in that of the other metals are seen to be short. Hence, Lockyer concludes, we are justified in assuming that the short lines seen in the spectra of the above metals to be coincident with long and strong lines of calcium, are really due to traces of the latter metal occurring in the former as an impurity.

*On the Spectrum of the Bessemer-Flame.*—Recent observations made by Dr. W. Marshall Watts at the Barrow Hematite Iron and Steel Company's Works (*Phil. Mag.* [4], 45. p. 81, 1873), prove that the peculiar lines seen in the spectrum of the Bessemer flame are due to the presence of an oxide of manganese, and not, as was previously and on good ground supposed, to that of carbon. The results of these observations are given in a diagram which shows the spectrum on the scale of wave-lengths. With it are given upon the same scale the spectrum of iron, that of the flame obtained on adding the spiegel and that of oxide of manganese. A comparison of these drawings shows that the "spiegel-spectrum" is essentially the same as the Bessemer-spectrum, only further developed, and that the Bessemer-spectrum, whilst containing a few lines of



iron, sodium, and lithium, is essentially the spectrum of *oxide* of manganese. No lines certainly known to be produced by carbon have been observed. It has been repeatedly affirmed that the lines in the Bessemer-spectrum are due to metallic manganese, and this has been as frequently denied. The above experiments prove that no single coincidence is observed between the spark taken from manganese poles and the Bessemer-spectrum; but that if the spectrum of a manganese oxide is obtained by bringing pyrolusite, manganese chloride, or other manganese compound into the oxyhydrogen flame, the coincidence between the lines thus obtained and those of the Bessemer flame is so complete as to convince any one who sees them that the two spectra are identical. It is, however, singular that these bands should be seen with equal or nearly equal brightness when iron containing a mere trace of manganese is used as when a highly manganeseiferous iron is worked, and still more strange that this spectrum, which is not that of carbon, should disappear at the exact moment when all the carbon is burnt out. Possibly the point which it is necessary to hit is not that of the exact removal of the carbon, but that at which the injurious oxidation of the iron begins, and this takes place when the quantity of manganese becomes too small to combine with the excess of oxygen.

*On the Carbon Spectrum.*—W. M. Watts (*Phil. Mag.* [4], xlviii. 456) has shown that the so-called second spectrum of carbon, obtained by passing the induction spark through tubes containing carbonic oxide, carbonic acid, or olefiant gas, is in reality the spectrum of an oxide of carbon. For when the gases giving this spectrum are heated with metallic sodium, the spectrum changes to that known as the first carbon spectrum, whilst if oxygen be again introduced, the bands characteristic of the second carbon spectrum reappear.

*On the Spectrum of the Aurora Borealis.*—The late Professor Angström, to whom this branch of science owes so much, has recently shown that a spectrum containing at least three of the lines of the aurora (viz. 428.6, 470.3, and 522.6) can be obtained by passing an induction discharge through a partial air-vacuum over powdered phosphate of lime. A violet light thus obtained, similar to that which is usually seen only at the negative pole, fills the flask, and gives the following lines—427.2, 470.7, and 522.7. A red line about 630 and the bright yellow band are not thus obtained, and the only way in which Angström can account for this is that it probably owes its existence to phosphorescence or fluorescence. The spectrum of the aurora is composed, according to Angström, of two distinct spectra; one consisting of this homogeneous yellow light and the other of extremely feeble bands of light seen only in the strongest auroral displays. H. C. Vogel, who has also recently carefully examined the aurora-spectrum, has come to the conclusion that it is to be regarded as a modified air-spectrum.

A. S. Herschel (*Phil. Mag.* xlix. 65) gives an account of the aurora-spectrum. J. R. Capron (*ibid.* xlix. 249) has also made comparisons of other spectra with the spectrum of the aurora, as the results of which he concludes that much yet remains to be done before we can positively decide as to the exact nature of the aurora-spectrum.

*Cometary Spectra.*—Huggins has shown that observations on the spectra of five small comets examined in the years 1866, 1868, and 1871, led to the conclusion that a great part of the light of these comets was not reflected solar light, but light emitted by the matter of the comet, and that the coincidence existing between the three bright bands seen in the spectra of three of these comets and the bright lines of carbon compounds, seemed to indicate the presence of that body in some form in the cometary matter. Coggia's comet (visible in July 1874, *Proc. Roy. Soc.* xxiii. 154) is the first bright comet whose spectrum has been thus examined, and this exhibited three spectra, viz. :—

1. A spectrum of three bright bands similar in position and character to those seen in other comets, and these bands could be resolved into lines which were not exactly identical in position with the bright lines of carbon (spark in olefiant gas), all the cometary bands being shifted towards the blue. Supposing that the comet's bands are identical with those of carbon, the observed shift would indicate a relative motion of approach of comet and earth of about 40 miles a second, a velocity nearly double of their actual relative motion. Another point which renders the conclusion doubtful is that the lines of this comet are due to carbon is that the bright line near G, seen in all carbon spectra, was not observed in the spectrum of the comet.

2. A continuous spectrum of the nucleus in which no dark lines or bright lines, other than the above-mentioned three bands, could be seen.

3. A continuous spectrum which accompanies the gaseous spectrum in the coma, which represents almost entirely the light of the tail, and is partly due to reflected sunlight, as a portion of the light is polarized, and partly probably derived from the comet itself.

The difficulty which presents itself in accounting for sufficient heat to maintain this

matter and the nucleus in a state of incandescence has also to be encountered in respect of the gaseous matter, which emits the light and is resolved into bright bands.

Renvier (*Compt. rend.*) has shown that striped muscular fibre acts as a diffraction grating, and on this principle he has constructed a 'muscle spectroscope.'

**SPINEL.** Pseudomorphs of spinel after chlorite from the district of Slatoust in the Ural were found by v. Kokscharow a. Nikolajew (*Jahrb. f. Min.* 1870, 102) to contain

SiO <sup>a</sup>	Al <sup>a</sup> O <sup>a</sup>	FeO	MgO
2.96	68.96	18.01	10.82 = 100.75.

**SPIRIT.** The 'first runnings' of the distillate obtained in the manufacture of alcohol from sugar-beet, and from molasses, consist chiefly of aldehyde, together with paraldehyde and metaldehyde; they also contain crotonic aldehyde, and, according to Krämer a. Pinner, acetal (see ALDEHYDE, p. 32).

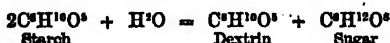
**STAFFELITE.** This calcic phosphate, occurring together with carbonate fluoride, &c., on phosphorite at Staffel, and in other localities (1st Suppl. 1037), is by some mineralogists regarded merely as an impure apatite (see *Jahresb. f. Chem.* 1870, 1317; 1871, 1172).

#### STANNIC COMPOUNDS. See TIN.

**STARCH.** On the structure of starch-grains, see Hartig (*Wien Akad. Ber.* [2ts. Abth.] lxiii, 805); *Jahresb. f. Chem.* 1871, 789).

On the size of starch-grains, see Schönn (*Dingl. pol. J.* cxv, 460; *Jahresb.* 1870, 1189); Hock (*ibid.* 1872, 1021). On the morphology of starch-grains: Hock (*Wiesner's Mikroskopische Untersuchungen*, pp. 55, 71; *Jahresb.* 1872, 1021).

**Reactions:** 1. With *Diastase.* According to Schulze a. Märker (*Dingl. pol. J.* cxi, 246), the ferment of malt-extract does not, like sulphuric acid, convert the whole of a given quantity of starch into sugar, but only the half of it. They conclude from their experiments that the action of diastase consists in the formation of a definite compound of sugar and dextrin, according to the equation:



O'Sullivan (*Chem. Soc. J.* [2], x, 581) finds that the ultimate product of the action of malt-extract on starch is maltose (v. 798), a sugar isomeric with milk-sugar, and capable, according to his observations, of reducing only two-thirds the quantity of cupric oxide that is reduced by dextroglucose (p. 766). By the prolonged action of acids, this sugar is completely converted into dextroglucose. On the action of malt-extract on starch, see also Schwarzer (*J. pr. Chem.* [2], i, 212; *Jahresb.* 1870, 854) and Contarot (*Compt. rend.* lxx, 282; *Jahresb.* 1870, 1195).

2. With *Acetic Anhydride.*—Starch-powder heated to 140° with about three times its weight of acetic anhydride containing 10 to 15 p.c. of acetic acid, swells up to a mass which, when washed with water, yields triacetyl-amidin,  $C^6H^7(C^2H^3O)^3O$ , a white powder, insoluble in water, alcohol, ether, and glacial acetic acid, not coloured blue by iodine, and reconverted by saponification into the original insoluble starch, which gives the blue reaction with iodine. If the mixture of starch and acetic anhydride is heated to 150°, a triacetyl-amidin is also formed, insoluble in water, alcohol, and ether, but differing from the former in being soluble in glacial acetic acid, and in yielding by saponification soluble starch. At higher temperatures a similar triacetyl-amidin is also formed, which, however, is converted by saponification into dextrin (Schützenberger, *Ann. Chim. Phys.* [4], xxi, 235).

3. With *Iodine.*—According to Duclaux (*Ann. Chim. Phys.* [4], xxv, 264; *Compt. rend.* lxxiv, 533) the formation of iodide of starch is a physical process, analogous to the absorption of lead-salts by charcoal. This conclusion is based on the following facts: a. The composition of iodide of starch is not constant. b. When iodine is added to an aqueous solution of starch, it does not act on the starch till the water has taken up a certain quantity of the iodine in the free state—that is to say, the iodine first dissolves in the water, then becomes divided between the water and the starch, and then only does the blue colour appear. c. The quantities of iodine which must be present in the water to produce the colour vary, under otherwise similar circumstances, with the temperature, and this explains the decoloration of iodide of starch by heat. d. The time at which the iodine begins to act upon the starch may often be accelerated or retarded by scarcely recognisable causes, in which no chemical action can be assigned.

c. The establishment of a state of equilibrium between iodine, starch and water depends upon the time, just like the absorption which is produced by charcoal.

The reactions of starch with iodine and with tannic acid have been examined by Griessmayer (*Ann. Ch. Pharm.* cli. 40; *Chem. Soc. J.* [2], x. 72), who finds that filtered starch-paste is in a state of continual change, being converted in about a week into a dextrin which gives a red colour with iodine, then in two or three days more into a dextrin which gives no coloration with iodine,—further into sugar, and finally into acid products. Tannic acid added in excess produces a precipitate as long as any unaltered starch is present, this precipitate disappearing on warming the liquid, and re-appearing on cooling.

On the reaction of starch with iodine in presence of dextrin, see O. Knab (*Chem. Centr.* 1872, 492, 508; *Jahresb.* 1872, 928).

4. With Aniline.—Starch heated with aniline is converted into dextrin (Schiff, *Deut. Chem. Ges. Ber.* iv. 908).

**Animal Starch.**—Granules exhibiting the physical and chemical characters of starch have been found by Daresto in the yolk of the hen's egg (*Compt. rend.* lxxii. 845; *Chem. Soc. J.* [2], lx. 838); also in the testicles, from which they disappear during the time of the formation of spermatozoa (*Compt. rend.* lxxiv. 131).

**STARCH-SYRUP and STARCH-SUGAR.** According to Krötke (*Dingl. pol. J.* cxix. 139), the addition of two ounces of strong nitric acid for every pound of sulphuric acid employed in converting starch into sugar, diminishes the time of boiling by one-half.

**STASSFURTITE.** See BORACITE (p. 206).

**STILBENE or TOLUYLENE**,  $C^{14}H^{12} = C^6H^3-CH=CH-C^6H^3$ . This hydrocarbon is found amongst the products of the dry distillation of Peru balsam (Kraut, *Arch. Pharm.* [2], cxli. 113).

It is formed in the decomposition of dibenzyl,  $C^{14}H^{14}$ , by heat (p. 177).

Stilbene crystallises in monoclinic forms, having the axial ratio:

Clino-diagonal	Ortho-diagonal	Principal axes
2.1561	1	1.8549.

Angle of inclined axes =  $113^{\circ} 22'$ .

Combination:  $\infty P : \infty P\infty . 0P . P\infty . \frac{2}{3}P\infty$ . Angle  $\infty P : \infty P = 126^{\circ} 20'$ ;  $\infty P : 0P = 100^{\circ} 23'$ ;  $\infty P : P\infty = 101^{\circ} 42'$ ;  $\infty P : \frac{2}{3}P\infty = 116^{\circ} 52'$ ;  $0P : P\infty = 129^{\circ} 46'$ ;  $\infty P\infty : \frac{2}{3}P\infty = 134^{\circ} 7'$ ;  $\frac{2}{3}P\infty : \infty P = 108^{\circ} 31'$  (G. vom Rath, *Deut. Chem. Ges. Ber.* v. 622).

Stilbene, heated for some time to  $150^{\circ}$ – $160^{\circ}$  with fuming hydrobromic acid, takes up bromine and hydrogen, forming a compound probably represented by the formula,  $C^6H^3-CHBr-CH^3-C^6H^3$  (Zincke, *Deut. Chem. Ges. Ber.* v. 342).

Stilbene, oxidised by chromic acid, is converted into benzoic aldehyde and benzoic acid (p. 175).

**STILBENE ALCOHOL.** The name given by Limpricht a. Schwanert to Zinin's hydrobenzoin,  $C^{14}H^{14}O^2$  (p. 172).

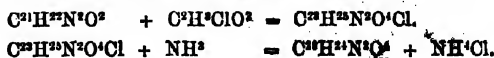
**STIRLINGITE.** This name is given by Konngott (*Jahrbuch f. Mineralogie*, 1872, 188) to a zinc chrysolite from Stirling Hill, Sussex County, New Jersey, analysed by W. T. Roepper (*ibid.* 1870, 392), and formerly regarded by him as tephroite. It occurs, with willemite, franklinite, jeffersonite, and spinel, in rhombic crystals two inches long, having the faces  $\infty P^2$ ,  $P\infty$ ,  $\infty P\infty$  predominant, and  $2P\infty$ ,  $P$ ,  $2P^4$  (?) subordinated. Hardness = 5.5 to 6. Sp. gr. = 3.95 to 4.08. Dark green to black. Analyses 1 and 2 were made on carefully selected cleavage specimens; 3 on a massive variety:

	SiO <sup>2</sup>	FeO	MnO	ZnO	MgO	X*	
1.	30.76	33.78	16.25	10.96	7.60	—	= 99.35
2a.	29.90	35.60	16.90	10.66	5.81	1.03	= 99.90
b.	30.68	35.44	16.93	10.70	5.44	1.04	= 100.11
3a.	30.67	35.37	17.81	9.87	5.69	1.39	= 100.80
b.	30.42	34.20	17.67	9.09	6.49	2.65	= 100.52

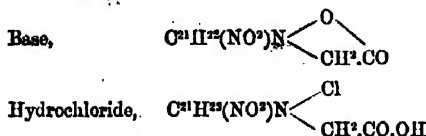
**STRYCHNINE**,  $C^{21}H^{27}N^3O^2$ . **Reactions:** 1. With Cyanides.—Potassium cyanide added to a strychnine solution throws down the pure base: strychnine does not, indeed, appear to form a hydrocyanide (Flückiger, *N. Jahrb. Pharm.* xxxviii. 138; Weith, *Deut. Chem. Ges. Ber.* iv. 527).

Insoluble residues (admixed spinel).

2. With *Chloracetic acid*.—On heating 3 pts. of finely powdered strychnine with 1 pt. of chloracetic acid to  $180^{\circ}$  for some hours, dissolving in water, and adding excess of ammonia, some unaltered strychnine separates, whilst the filtrate contains a new base,  $C^{21}H^{22}N^2O^2$ , which on evaporation is obtained in groups of white silky needles, readily soluble in hot water and alcohol, but not in ether. The solution has a neutral reaction. The formation of this compound is explained by the equations:



The nitrate and oxalate are very sparingly soluble in water. The solution of the base gives with potassium chromate a yellow crystalline precipitate, and with silver nitrate a silver compound crystallising in long colourless needles. It is also precipitated by bromine-water and tannic acid. With potassium chromate and sulphuric acid it gives the strychnine reaction. Subcutaneous injections of it produce tetanus in frogs. The constitution of this base and of its hydrochloride may be expressed as follows:



(F. Roemer, *Zeitschrift f. Chem.* 1871, 435).

3. With *Pernanganic acid*.—Wenzel (*Zeitschr. anal. Chem.* 1871, 226) recommends, as the most delicate test for strychnine, a solution of 1 pt. potassium permanganate in 2,000 pts. sulphuric acid, which produces a green colour, contrasting very strongly with the purple-red of the aqueous solution.

4. With *Cerozo-ceric oxide*.—See ALKALOIDS (p. 43).

5. On the separation of strychnine and *morphine*, see p. 818.

*Periodides of Strychnine*.—The following have been prepared by Jørgensen (*J. pr. Chem.* [2], iii. 145; compare 1st *Suppl.* 1039):

Strychnine tri-iodide, $C^{21}H^{22}N^2O^2.HI^3$	} Crystals of the rhombic system.
Methyl-strychnine tri-iodide, $C^{23}H^{25}N^2O^2.CH^3.I^3$	
Ethyl-strychnine tri-iodide, $C^{25}H^{28}N^2O^2.C^2H^5.I^3$	} Red-brown plates having an adamantine lustre. Sparingly soluble even in boiling alcohol.
Bromethylene-strychnine tri-iodide, $C^{21}H^{22}N^2O^2.C^2H^4Br.I^3$	
Amyl-strychnine tri-iodide, $C^{21}H^{22}N^2O^2.C^4H^{11}.I^3$	} Shining brown laminae, isomorphous with the ethyl-compound.
Amyl-strychnine pentioidide, $C^{21}H^{22}N^2O^2.C^4H^{11}.I^5$	

Neither methyl-, ethyl-, nor bromethylene-strychnine, nor strychnine itself, appears to form a pentioidide.

*Cobaltocyanide of Strychnine* forms well-defined crystals having the composition  $Co^2Cy^{12}(C^{21}H^{22}N^2O^2)H^4 + 8H^2O$ . The *Nickelocyanide* has the composition  $Ni^2Cy^{12}(C^{21}H^{22}N^2O^2)H^4 + 10H^2O$  (R. H. Lee, *Deut. Chem. Ges. Ber.* iv. 789).

**Oxethyl-Strychnine**,  $C^{23}H^{25}N^2O^2 = C^{21}H^{22}(OO^2H^3)N^2O^2$ . (R. Meissel, *Ann. Ch. Pharm.* clvii. 7). The *hydrochloride* of this base is formed by heating 10 grams of pulverised strychnine with 2.4 grams of the hydrochloride of ethylene-oxide,  $C^2H^4.O.HCl$ , and alcohol in a sealed tube to  $120^{\circ}$ – $160^{\circ}$  for about a day. On subsequently rinsing the tube with alcohol, expelling the alcohol by evaporation, and treating the residue with water, a small quantity of unaltered strychnine remains undissolved, while the easily soluble *oxethyl-strychnine hydrochloride*,  $C^{23}H^{25}N^2O^2.HCl + H^2O$ , separates from the concentrated solution in white silky needles. This salt has a sweet taste, with bitter after-taste; in a very dilute solution the sweet taste alone is perceptible. It exerts a strong paralyzing action on the motor nerves.

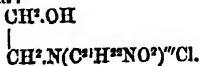
The solutions, even when very dilute, give with *platinic chloride* a crystalline double salt having a fine orange-red colour. *Potassium chromate* and *strong sulphuric acid* colour the aqueous solution violet, the colour disappearing after long standing. By boiling with strong *sulphuric acid*, the same reaction is obtained as with *strychnine*.

Dilute *nitric acid* forms with the solution of the hydrochloride, after addition of water, a yellow liquid which is turned red by stannous chloride. A strong solution of the chloride forms with *potassium sulphocyanate*, after 12 hours, large transparent crystals; with *potassium iodide*, long transparent needles.

**Oxethyl-strychnine nitrate** is obtained in hard, needle-shaped crystals, by precipitating the solution of the hydrochloride with silver nitrate. The *sulphate*, obtained by boiling the chloride with silver sulphate, forms large white crystals containing  $(C_{28}H_{27}N_2O_3)SO_4 \cdot 2H_2O$ .

**Oacetyl-Strychnine hydroxide**,  $C^{28}H^{42}N^2O^4$ , is best prepared by precipitating the sulphate with a boiling saturated solution of baryta, removing the excess of baryta with a few bubbles of carbonic anhydride, evaporating, exhausting with alcohol, and precipitating the solution with ether. A small quantity of a brown amorphous body is then deposited, and adheres closely to the sides of the vessel, so that the nearly decolorised liquid can be decanted off clear, and, on further addition of ether, especially on agitation, the free base separates in small tufts of dazzling white crystals.

For the hydrochloride of oxethyl-strychnine, Messel suggests (from analogy with *pholine*) the structural formula:



**STYPHENIC ACID.** Syn. with TRINITRO-RESORCIN, see RESORCIN (p. 1043)\*.

**STYROL** or **CINNAMENE**,  $C^8H^8 = C^6H^5-CH=CH^2$ . When secondary ethyl-benzyl alcohol,  $C^8H^9-CH(OH)-CH^3$  (obtained by treating a solution of acetophenone in dilute alcohol with sodium-amalgam) is heated for some time with zinc chloride in a vessel with reversed condenser, water is given up, and on subsequent distillation, a liquid passes over containing a large quantity of benzene, and yielding after repeated fractionation, a small quantity of a liquid which boils between  $144^\circ$  and  $160^\circ$ , and exhibits the properties of styrol from storax. Styrol appears also to be produced, and in larger quantity, by the action of alcoholic potash on chloretethylbenzene,  $C^6H^5-CHCl-CH^3$  (Emmerling & Engler, *Deut. Chem. Ges. Ber.* iv. 147).

163). *Bromostyrols* or *Bromocinnamenes* (C. Glaser, *Ann. Ch. Pharm.* cliv.

163). *α*-Bromostyrol,  $\text{C}_6\text{H}_5\text{—CH=CHBr}$ , is formed from styrol dibromide, by heating with alcoholic potash; it is a yellowish, heavy oil, not volatile without decomposition, and having a sharp, tear-exciting odour. Heated to  $120^\circ$  with concentrated alcoholic potash, it yields acetenyl-benzene.

$\beta$ -Bromostyrol,  $C^9H^7Br$ , is produced from phenyl-dibromopropionic acid (1st Suppl. 470) by heating with water; by the action of bromine on warm aqueous solutions of alkaline cinnamates; and by heating phenyl-bromolactic acid with water to 200°. It forms a light yellow oil, which boils without decomposition at 228°, and has a fine hyacinth odour. With nitric acid, it forms benzoic acid; it is not decomposed by alcoholic potash or potassium cyanide. (Glasgow, loc. cit.)— $\alpha$ -Chlorostyrol,

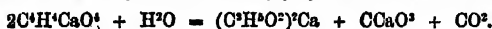
*Chlorostyrols* or *Chlorocinnamenes* (Glaser, *loc. cit.*)— $\alpha$ -Chlorostyrol,  $\text{C}_6\text{H}_5\text{—CH=CHCl}$ , is the compound obtained by Blyth & Hofmann (*Ann. Ch. Pharm.* liii. 292).— $\beta$ -Chlorostyrol,  $\text{C}_6\text{H}_5\text{—CCl=CH}_2$ , is the compound which Stenhouse obtained by treating alkaline solutions of cinnamic acid with chlorine (*ibid.* lv. 3 and lvii. 70). Glaser obtained it as a bye-product in the preparation of phenyl-chlorolactic acid (*Jahresb. f. Chem.* 1867, 418); it may also be produced by heating phenyl-chloro-lactic acid with water to  $200^\circ\text{--}220^\circ$ . In the pure state it is a colourless oil, having an agreeable odour of hyacinth, boiling at  $199^\circ$  under a pressure of 766 mm. and at  $119^\circ$  under a pressure of 40 mm. Sp. gr. =  $1.112$  at  $22.3^\circ$ . By oxidation, it yields benzoic acid. On heating it with alcoholic potash and with potassium cyanide to  $200^\circ\text{--}250^\circ$ , partial resinisation takes place, but no chloride of potassium is formed.

**SUBERIC ACID,  $C_8H_{14}O_4$ .** This acid, heated to  $160^\circ$  with the required quantities of bromine, is converted into monobromosuberic acid,  $C_8H_{13}BrO_4$ , and dibromosuberic acid,  $C_8H_{12}Br_2O_4$ ; and these acids, boiled with potash and treated with alcohol, yield suberomalic acid,  $C_8H_{12}O_6$ , and suberotartronic acid,  $C_8H_{10}O_6$ , both uncrystallisable and forming salts which crystallise with difficulty (H. Gal. & J. Gay-Lussac, *Compt. rend.*, lxx. 1175).

**SUCCINIC ACID**,  $C^4H^4O^4 = C^4H^4(COOH)^2$ . *Alleged occurrence in Urine.*—The statement of Meissner a. Joly (v. 453), that succinic acid is found in the urine of dogs fed on flesh and fat, is contradicted by E. Salkowski (*Pfugers Archiv. f. Physiologie*, iv. 21), who obtained no indication of its presence in the urine of a dog fed for a month on a copious diet of flesh and fat, although the detection of it is easy. His experiments likewise indicate that this acid does not occur in human urine.

*Formation.*—Wippermann (*Deut. Chem. Ges. Ber.* iii. 337) has obtained succinic acid, together with other products, by the action of ethylic dibromacetate on the mixture of sodacetic ethers which Frankland a. Duppa obtained by the water of sodium on ethyl acetate.

*Succinates.*—According to Béchamp (*Compt. rend.* lxx. 909), calcium succinate fermented in contact with microzyme chalk (1st Suppl. 614) and a small quantity of meat, yields not a trace of hydrogen, but only propionic and carbonic acids:



According to Lutschak (*Deut. Chem. Ges. Ber.* v. 30), zinc succinate is capable of uniting with 3 mols. ammonia, forming the compound  $C^4H^4ZnO^2.3NH^3$ .

**SUCCINIC AMIDES AND ANILIDES.** (Menschutkin, *Ann. Ch. Pharm.* cxlii. 165, 187).

*Succinimide*,  $C^4H^4O^2.NH$  =  $C^4H^4 \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} NH$ , is obtained in satisfactory

quantity by distilling ammonium succinate as quickly as possible. It boils at  $237^{\circ}$ – $288^{\circ}$ , leaving a small residue of charcoal. The hydrogen of succinimide is replaceable only by silver or mercury. *Argento-succinimide*,  $C^4H^4O^2.NAg$ , has been already described (v. 461). In the hydrated compound,  $2(C^4H^4O^2.NAg) + H^2O$ , the water does not appear to exist as water of crystallisation.

*Mercurio-succinimide*,  $(C^4H^4O^2.N)^2Hg$ , formed on dissolving mercuric oxide in a hot aqueous solution of succinimide, is moderately soluble in alcohol, extremely soluble in cold water, and crystallises therefrom in long needles having a silky lustre.

On adding solution of mercuric chloride to an aqueous solution of mercurio-succinimide, a precipitate is formed, consisting of microscopic, shining, rhombic tables, less soluble in water than mercurio-succinimide itself, and represented by the formula  $(C^4H^4O^2.N)^2Hg.HgCl$ .

*Succinamide*,  $C^4H^4O^2(NH^2)^2$ , is formed by the action of alcoholic ammonia on succinimide even at ordinary temperatures, but more quickly by heating the materials together to  $100^{\circ}$  in a sealed tube for several hours.

*Mercurio-succinamide*,  $C^4H^4O^2(NH^2)^2.HgO + \frac{1}{2}H^2O$ , is formed on dissolving recently prepared mercuric oxide in a boiling aqueous solution of succinamide, and separates on cooling as a white powder.

*Succinamates.*—The ammonium salt remains in the alcoholic mother-liquor of succinamide obtained as just described, when the alcohol used contains water. The calcium salt,  $(C^4H^4NO^2)^2Ca$ , is formed by boiling succinamide with milk of lime, and separates on passing carbonic anhydride into the filtrate, evaporating over the water-bath, and adding alcohol, as a pulverulent crystalline precipitate, or in stellate groups of short prisms; from dilute solutions in long needles.

*Succinanil or Phenylsuccinimide* may be conveniently prepared by pouring aniline (1 mol.) on succinic acid (1 mol.) in a retort, heating gradually, and as soon as the boiling ceases, distilling the succinanil over at a stronger heat. It may be purified by recrystallisation from water or alcohol; and by dissolving it in strong sulphuric acid, precipitating with water and recrystallising from alcohol, it may be obtained perfectly colourless, in needles, or in long, thin, strongly refracting prisms. It melts at  $166^{\circ}$ , is nearly insoluble in cold, sparingly soluble in boiling water, more easily in boiling alcohol; boils above  $300^{\circ}$  without decomposition.

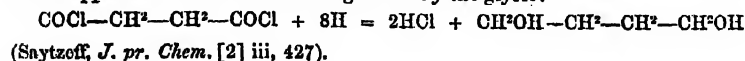
*Succinanilic or Phenylsuccinamic acid.*—The barium salt of this acid,  $(C^6H^5NO^2)^2Ba + 3H^2O$ , is obtained by dissolving succinanil in boiling baryta-water, removing the excess of baryta by carbonic acid, and concentrating, in suits of crystalline needles having a satiny lustre, easily soluble in water, and giving off their water of crystallisation at  $110^{\circ}$ . The calcium salt,  $(C^6H^5NO^2)^2Ca + 4H^2O$ , and the lead salt, prepared in like manner, crystallise in needles. The silver salt,  $C^6H^5NO^2Ag$ , is obtained by double decomposition, as a precipitate, which quickly becomes crystalline, dissolves with difficulty in boiling water, and crystallises therefrom in anhydrous prismatic crystals. Free succinanilic acid,  $C^6H^5O^2(C^6H^5NH)OH$ , is obtained by precipitating the calcium salt with hydrochloric acid, and recrystallising the precipitate

from boiling water, in small concentrically grouped needles, which are nearly insoluble in cold water, but dissolve easily in alcohol and in boiling water. The acid melts at  $148.5^{\circ}$ , and is resolved at a higher temperature into water and succinil. It does not give off aniline when treated with aqueous potash.

**Phenylsuccinamides.**—*Monophenylsuccinamide*,  $C^6H_5O^2\{NH^2\}NHC^6H_5$ , is formed, together with a small quantity of ammonium succinilate, by heating succinil with alcoholic ammonia. It crystallises from water in broad needles, dissolves with moderate facility in hot water, sparingly in alcohol, melts at  $181^{\circ}$ , and forms a very sparingly soluble compound with mercuric oxide. Quicklime converts it into succinilic acid.

*Diphenylsuccinamide* or *Succinilide*,  $C^{12}H^{10}O^2(NHC^6H_5)^2$ , is obtained as a by-product in the preparation of succinil. The portion insoluble in water may be crystallised from alcohol, then boiled with alcoholic potash, and purified by recrystallisation. It crystallises from alcohol in broad, flat, shining needles, which melt at  $226.5^{\circ}$  to  $227^{\circ}$ . It is very stable, dissolves in nitric and sulphuric acids, and is precipitated therefrom by water without alteration. When heated to  $100^{\circ}$  in a sealed tube with strong hydrochloric acid, it is resolved into aniline and succinic acid, and when distilled, it splits up into aniline and succinil.

**SUCCINIC CHLORIDE**,  $COCl-CH^2-CH^2-COCl$ . This compound, mixed with acetic acid, and treated with sodium-amalgam, is converted into a butylene glycol, which appears to be the true homologue of ethylene glycol:



**SUCCINYLBENZAMIC ACIDS.** By fusing succinic acid with amidobenzoic acid, two acids are obtained, namely, succinylbenzamic acid,  $C^{11}H^7\{N(C^6H^4O^2)^2\}COOH$ , which is soluble in water, and melts at  $235^{\circ}$ , and succinyldibenzamic acid,  $C^{12}H^8O^2(NH.C^6H^4O^2)^2$ , which is insoluble in water. The former is an imidogen acid, and is converted, by fixation of water, into oxysuccinylbenzamic acid,  $C^{11}H^7\{NH.C^6H^4O^2.OH\}COOH$ . The second acid is also produced by heating the first with amidobenzoic acid (Muretow, *Deut. Chem. Ges. Ber.* v. 330).

**SUCCINYLBENZOLIN**,  $(C^{11}H^{11}O^2)^2.C^6H^5O^2$ , is formed by the action of succinic chloride on benzoin. It crystallises from alcohol in shining leaflets; is insoluble in water, but soluble in alcohol ether and carbon sulphide; melts at  $129^{\circ}$ ; and is converted by alcoholic potash into benzilic and succinic acids (A. Lukanin, *Deut. Chem. Ges. Ber.* v. 331).

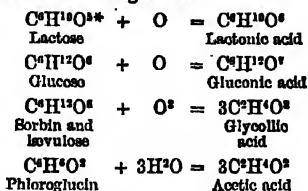
**SUCCINYLBENZOLINE-SULPHAMIDE**,  $N^2H^2(C^6H^4SO^2)(C^6H^5O^2)$ . See **TOLUENE-SULPHAMIDES** (p. 1168).

**SUGARS.** 1. *Reaction with Chlorine and Water.*—Hlasiwetz & Barth, in 1861, by treating milk-sugar with bromine and water, obtained a brominated compound which, when decomposed by bases, yielded isodiglycolethyleneic acid,  $C^6H^{10}O^4$  (iii. 414, 1023). The same treatment has more recently been applied by Hlasiwetz & Habermann (*Ann. Ch. Pharm.* clv. 120) to other kinds of sugar. The results show that the capability of a sugar to form such an acid containing the same number of carbon-atoms in itself, increases with the fermentability of the sugar, non-fermentable or difficultly fermentable sugars being converted by this process into acids containing smaller numbers of carbon-atoms.

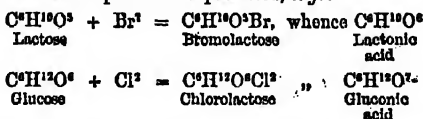
Moderately dilute solutions of sugars were treated with chlorine gas, as long as it continued to be absorbed, the action in the case of rather large quantities going on for four or five days. The liquid was then freed from chlorine by drawing air through it, warmed in a dish, and a magma of silver oxide added to it till the liquid became neutral. It was then filtered, the undissolved matter washed for a long time with neutral water; the filtrates, which generally began to grow brown and turbid from reduced silver, were immediately treated with hydrogen sulphide; and the mostly limpid acid liquids filtered from the silver sulphide were concentrated on the water-bath. From the crude acids thus obtained, mostly containing more or less undecomposed sugar, the calcium salts were prepared, and from these, through the medium of the lead salts, the free acids were obtained.

Cane-sugar and dextroglucose yield gluconic acid,  $C^6H^{12}O^7$  (p. 550), differing by  $H^2O$  from lauronic or isodiglycolethyleneic acid from milk-sugar. Levulose and by  $H^2O$  from lauronic or isodiglycolethyleneic acid from milk-sugar. Levulose and by  $H^2O$  from lauronic or isodiglycolethyleneic acid from milk-sugar. Diarsorbin yield glycollic acid. Phloroglucin yields dichloroacetic acid. Diarsorbin yield glycollic acid. Phloroglucin yields dichloroacetic acid.

garding the intermediate products, and reducing the process to its simplest expression, the four following cases are to be distinguished:



The chlorine or bromine in these reactions appears to be simply added on to the sugar-molecule, and the acid to be formed by substitution of O for Cl<sup>2</sup> or Br<sup>2</sup> in the chlorinated or brominated compound thus produced, e. g.:



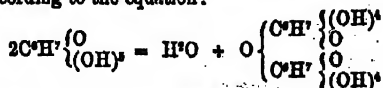
These sugars behave then like unsaturated compounds, as indeed Linnemann has shown to be the case with dextroglucose, which by taking up H<sup>2</sup> is converted into mannite (iii. 823).

2. *Action of Nascent Hydrogen.*—Bouchardat (*Compt. rend.* lxxiii. 199, 1008) has shown that cane-sugar, glucose, and milk-sugar are converted by the action of sodium-amalgam in presence of water into mannite or dulcite, and a certain number of monatomic alcohols, viz., ethyl alcohol, isopropyl alcohol, and a hexyl alcohol identical with that which Erlenmeyer and Wanklyn obtained from mannite and dulcite. Dextroglucose treated in this manner yields the three volatile alcohols just mentioned, together with mannite; milk-sugar the same volatile products, together with dulcite; inverted milk-sugar a mixture of mannite and dulcite.

3. *Reactions with Acetic Anhydride.*—The products obtained by the action of acetic anhydride on glucose and cane-sugar, according to the latest investigations of Schützenberger (*Ann. Ch. Pharm.* [4], xxi. 235) differ in some respects from those described in the *First Supplement* (p. 1045).

1. Pure crystallised dextroglucose dried at 100° is easily attacked by acetic anhydride at 120°, the products differing according to the proportions used. One part of glucose and 2½ pts. of anhydride heated in an open vessel react readily, the action being over in a few moments; a little water being added to destroy the anhydride, and the whole evaporated to dryness on the water-bath an amorphous residue soluble in water, and of a very bitter taste, is obtained. Boiling benzene only partly dissolves this residue, the soluble part being triacetyl-glucose, C<sup>6</sup>H<sup>7</sup>(C<sup>2</sup>H<sup>3</sup>O)<sup>3</sup>O<sup>8</sup>. This body, heated to 140° by itself or with acetic anhydride, loses water, giving triacetyl-glucosan, C<sup>6</sup>H<sup>7</sup>(C<sup>2</sup>H<sup>3</sup>O)<sup>3</sup>O<sup>5</sup>, insoluble in water, soluble in dilute acetic acid. The insoluble part dissolved in water, and decolorised by animal charcoal, yields, on evaporation in a vacuum, an amorphous, light yellow, bitter mass, very soluble in water, and soluble in alcohol; this is diacetyl-glucose, C<sup>6</sup>H<sup>9</sup>(C<sup>2</sup>H<sup>3</sup>O)<sup>2</sup>O<sup>8</sup>.

Glucose, heated with a large excess of anhydride to 160° for 6 hours, does not form a glucose-derivative, but one derived from two molecules of glucose, which coalesce with loss of H<sup>2</sup>O, according to the equation:



All the eight hydrogen-atoms of the hydroxyl present in this diglucose may be replaced by acetyl, forming C<sup>12</sup>H<sup>10</sup>O<sup>11</sup>, which is either identical or isomeric with the compounds of the same composition obtained by the action of acetic anhydride on cane- and milk-sugars; in water it is insoluble, in alcohol soluble; it has no marked taste of any kind.

All the acetylated derivatives of glucose are dextrorotatory.

2. Cane-sugar heated with ½ pt. acetic anhydride, and 3-4 pts. glacial acid, entirely

\* The old formula of milk-sugar is used in this equation merely to show more clearly the analogy of the reaction to that which takes place in the other cases. With the new formula, the equation would be: C<sup>12</sup>H<sup>22</sup>O<sup>11</sup> + O = H<sup>2</sup>O + C<sup>12</sup>H<sup>20</sup>O<sup>10</sup>.



dissolves; other throws down a yellow tarry precipitate, which, when dried in a vacuum over quicklime, and finally at 100°, is a solid substance soluble in water and alcohol, of a faint sweet taste, somewhat inclined to bitter, insoluble in ether and benzene; this is monoacetyl-saccharose,  $C^{12}H^{21}(C^2H^3O)O^{11}$ . The ethereal filtrate from this substance evaporated to dryness, dissolved in water, and decolourised by animal charcoal, gives numbers intermediate between those required for tetra- and penta-acetyl-saccharose, and is probably a mixture of these two bodies; it is soluble in water, alcohol, and ether.

Heated with a large excess of acetic anhydride, cane-sugar yields hepta- and octo-acetyl-saccharose,  $C^{12}H^{13}(C^2H^3O)^7O^{11}$  and  $C^{12}H^{14}(C^2H^3O)^8O^{11}$ , as gummy amorphous bodies insoluble in water, and much resembling the octoacetyl-diglucose obtained with glucose.

3. *Milk-sugar* is less easily acted on than cane-sugar; after long boiling, however, in an open vessel it dissolves completely. From the product water precipitates octo-acetyl-lactose,  $C^{12}H^{14}(C^2H^3O)^8O^{11}$ ; the solution contains tetra-acetyl-lactose, which forms indistinctly shaped crystals of a bitter taste; these bodies have the rotatory powers  $[\alpha] = +31^\circ$ , and  $[\alpha] = +50.1^\circ$  respectively.

On the Acetyl-derivatives of Mannite, see MANNITH (p. 774).

On the Synthesis of Glucosides by means of the Acetyl-derivatives of the Sugars, see pp. 560, 1088.

*Estimation of Sugars.*—1. Estimation and separation of Cane-sugar, Invert-sugar and Dextroglucose or Grape-sugar. The following method is given by J. Apjohn (*Chem. News*, xxi. 86; *Zeitschr. anal. Chem.* ix. 498). The amount of cane-sugar is first determined by the optical method, and then, after inversion, the sum of the three sugars. If then  $x$  denote the cane-sugar,  $y$  the grape-sugar, and  $z$  the invert-sugar, 0.24, 0.086, and 0.182 being the rotations produced in the polarising apparatus by 1 gram of cane-sugar, grape-sugar, and invert-sugar respectively, 1.16 the ratio between the half-molecular weight of the cane-sugar and that of the grape-sugar, and 1.1 that between the molecular weight of the invert-sugar and the grape-sugar, we have the equations:

$$\begin{aligned} 0.24x - 0.086y + 0.182z &= t \\ 1.16x + 1.1y + z &= w, \end{aligned}$$

from which the magnitudes  $y$  and  $z$  can be calculated.

Instead of determining the amount of cane-sugar by the optical method, which is difficult, as the syrup always acquires a more or less dark colour by inversion, the determination may be made by the chemical method. For this purpose it is merely necessary to test the syrup with copper-solution before and after inversion, the difference of the two determinations giving the amount of cane-sugar. The equations to be used are:

$$1.1y + z = w,$$

where  $w$  is the quantity of grape-sugar corresponding with  $y$  and  $z$ ; after inversion:

$$1.16x + 1.1y + z = w,$$

where  $w$  is the quantity of grape-sugar corresponding with  $x$ ,  $y$ , and  $z$ . Therefore:

$$x = \frac{w - w'}{1.16}.$$

The numbers obtained, according to these equations, from direct experiments, did not give perfectly accordant results. The discrepancy is attributed by Apjohn to the presence in the syrup of a substance different from the three kinds of sugar, but nevertheless capable of producing circular polarisation, and perhaps also of reducing copper solution, e.g. dextrin, asparagin, &c.

A. Dupré (*Chem. News*, xxi. 97; *Zeitschr. anal. Chem.* ix. 501) likewise estimates the three kinds of sugar above mentioned by a combination of the optical and chemical methods, which he regards as more direct than that of Apjohn. Cane-sugar does not reduce copper solution, and is not altered by heating it in solution with caustic alkalis, whereas grape- and fruit-sugar are completely destroyed. The cane-sugar may, therefore, be estimated by polarisation after the other kinds of sugar have been destroyed, and the other two sugars may be determined together by the chemical method, independently of the presence or absence of cane-sugar. It only remains, therefore, to determine the rotation produced by all the three sugars together, and we shall then have all the data required for the calculation. In a Jellet's instrument it was found that 1 p.c. cane-sugar required for compensation 0.2418 inch of levogyrate turpentine; 1 p.c. fruit-sugar required 1.502 inch of a 10 p.c. solution of cane-sugar; and 1 p.c. grape-sugar required 0.836 inch of the same solution of cane-sugar. If, then,  $x$  denotes the required quantity of fruit-sugar,  $y$  that of the grape-sugar,  $p$  the sum of

the two in percentages, as given by the copper-solution,  $a$  the number of inches of a 10 p.c. solution of cane-sugar which, according to observation, is required to compensate the mixture  $p$ , of fruit- and grape-sugar, or is equivalent thereto, we have the equations:

$$x + y = p$$

$$1.502x - 0.836y = \pm a$$

therefore,

$$x = \frac{0.836p + a}{2.338}$$

$$y = p - x.$$

The + sign is used for  $a$  when the mixture of the two sugars relates to the left; the - sign when the same mixture rotates to the right. Dupré has applied this method only to the estimation of sugar in wine, but he considers that it will be likewise applicable to cane-sugar and syrups.

On the examination of sugars containing Glucose, see also C. H. Gill (*Chem. Soc. J.* [2], ix. 91).

On the Decolorisation of Sugar solutions for Polarimetric Analysis, see Scheibler (*ibid.* [2], ix. 765) and Casamajor (*Chem. News*, xxv. 306; *Chem. Soc. J.* [2], x. 927).

On the estimation of Sugar by Copper solution, see F. Weil (*ibid.* [2], x. 1121).

On the use of Sodio-cupric glyceride (Glycerin-kupferoxydnatron) instead of sodio-cupric tartrate for the estimation of Glucose, see J. Löwo (*Zeitschr. anal. Chem.* ix. 20, 224; *Jahresb. f. Chem.* 1870, 1036).

On the estimation of Glucose in presence of Dextrin, see Schubert (*Zeitschr. anal. Chem.* ix. 112; *Jahresb.* 1870, 1038); also Rumpf a. Heinzerling (*Zeitschr. anal. Chem.* ix. 358; *Jahresb.* 1870, 1042).

On the estimation of Glucose by means of Mercuric Cyanide, see C. Knapp (*Ann. Ch. Pharm.* cliv. 252; *Jahresb.* 1870, 1033).

Comparison of the methods of Fehling, Knapp and Gentolo with Potassium Ferrocyanide for the estimation of Grape-sugar: *Jahresb.* 1870, 1034; *Chem. Soc. J.* [2], x. 829.

On the occurrence and estimation of Sugar in Wine, see Schubert (*Zeitschr. anal. Chem.* ix. 112; *Jahresb.* 1870, 1037). Estimation in Grape-juice: Pollack a. Pasquini (*J. Pharm. Chim.* [4], xi. 80; *Zeitschr. anal. Chem.* ix. 274; *Jahresb.* 1870, 1039); in Urine: Schubert (*Zeitschr. anal. Chem.* ix. 112; *Jahresb.* 1870, 1064); Seegen (*Pharm. J. Trans.* [3], ii. 202; *Chem. Soc. J.* [2], ix. 1005).

**Manufacture of Sugar.**—On the Extraction of Beet-juice by Diffusion, see Walkhoff (*J. pr. Chem.* cxxxiv. 149; *Jahresb. f. Chem.* 1867, 936); Duquesne a. Gil (*Dingl. pol. J.* cxvii. 83; *Jahresb.* 1870, 1198); Cech (*ibid.* cxvii. 278, 445; *Jahresb.* 1870, 1198). On a new Diffusion-apparatus for extracting the juice of any plant, especially of the Sugar-beet and Sugar-cane: J. Robert (*Dingl.* cci. 257). On Schultz's cold-diffusion-process (*ibid.* cci. 262; *Jahresb.* 1871, 1078).

On the Concentration of Sugar juices, see Cech (*Dingl.* cxviii. 428). On the use of Sulphurous acid in the Vacuum-apparatus: Seyffert (*ibid.* cxviii. 94; *Jahresb.* 1870, 1202; *Chem. News*, xxii. 248).

On the Refining of Sugar by means of 'hydrosacrocarbonate of lime': *Dingl.* cxvi. 84; *Jahresb.* 1870, 1204.

On the formation of Molasses and the influence of certain Salts, Organic and Inorganic, on the Crystallising power of Cane-sugar: Marschall (*Zeitschr. d. Vereine. Rübensuckerindustrie im Zollverein*, 1870, 52, 330; *Jahresb.* 1870, 1204; *Chem. Soc. J.* [2], ix. 456).

On the Recovery of Sugar from Molasses by means of Baryta: G. Lunge (*Dingl.* ccii. 164; *Chem. Soc. J.* [2], x. 185).

On the Separation of Iron oxide from Raw Sugar: *Dingl.* cciii. 325; *Chem. Soc. J.* [2], x. 530.

On the Manufacture of Starch-syrup and Starch-sugar, see Krätke (*Dingl. pol. J.* cc. 139; cciv. 243; *Jahresb. f. Chem.* 1871, 1076; 1872, 1022; *Chem. Soc. J.* [2], ix. 458).

**Cane-sugar or Saccharose.** On the specific heat of cane-sugar solutions, see Hnat (p. 601).

**Solubility in mixtures of Alcohol and Water.**—O. Scheibler (*Deut. Chem. Ges. Ber.* 1343) has investigated the solubility of cane-sugar in aqueous alcohol of different strengths and at different temperatures. Mixtures comparatively poor in alcohol dissolve more sugar than the water contained in them would dissolve by itself, but the more highly alcoholic mixtures the reverse is the case. The proportion in which alcohol neither promotes nor hinders the solution of sugar in water, is 46 p.c. by volume at 40°, and 50 p.c. at 14°. An aqueous solution of sugar saturated at 65°

tains 66 p.c. sugar; at 40°, 75½ p.c.; and at 14°, 66 p.c. The last-mentioned solution, when mixed with an equal volume of absolute alcohol, will still remain saturated at that temperature, but a further addition of alcohol causes the separation of sugar. Sugar is but very slightly soluble in alcohol of more than 90 p.c., and quite insoluble in absolute alcohol.

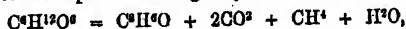
For the tabulated results, see the original paper.

**Action of Light.**—A solution of 10 grams of white cane-sugar in 50 grams of water enclosed in a sealed tube, from which the air had been expelled by boiling the liquid, and kept for five months exposed to light, was found to be about half converted into glucose. A similar solution kept for the same time in the dark remained unaltered (Raoult, *Compt. rend.* lxxiii. 1049).

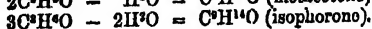
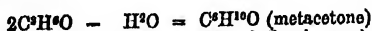
For Maumené's experiments on the action of water and heat, or of heat alone, upon cane-sugar, see *Bull. Soc. Chim.* [2], xvii. 442.

**Distillation with Lime.**—Frémy, by distilling sugar with quicklime, obtained a distillate consisting chiefly of metacetone,  $C^6H^{10}O$  (iii. 932). R. Benedikt (*Ann. Ch. Pharm.* clxii. 303), by distilling 1 pt. of sugar with 3 pts. of lime, as recommended by Gottlieb (*ibid.* lii. 127), obtains a distillate consisting of a watery and an oily layer. The watery layer contains acetone, together with a small quantity of acetic acid. The oily layer contains metacetone, boiling at 83°–84° (isomeric with mesityl oxide, b.p. 181°), and isophorone,  $C^9H^{14}O$ , boiling at 210°, yielding, when treated with phosphoric anhydride, a hydrocarbon having approximately the composition  $C^{12}H^{12}$ , but not identical with camene or with mesitylene.

Metacetone and phorone are the chief liquid products of the distillation of sugar with lime; they occur, however, only in small quantity in comparison with the gaseous products, which consist mainly of hydrocarbons. Benedikt gives, as a probable representation of the decomposition of sugar by lime, the equation:



and regards the metacetone and phorone as products of condensation of the acetone formed in the first instance:



The higher-boiling portions of the crude distillate probably contain still higher condensation-products of the same kind.

**Oxidation by Potassium Permanganate.**—Maumené (*Compt. rend.* lxxv. 85) finds that when a solution of 200 grams of permanganate, dissolved in 4 litres of water, is poured into a solution of 200 grams of sugar-candy in 2 litres of water, the mixture in fifteen to twenty minutes becomes heated to 45°–48°, manganic oxide separates in a lump, and a colourless neutral solution is formed, no longer sweet, but retaining its optical rotatory power unaltered. In this liquid Maumené, on the strength of a few qualitative reactions, assumes the existence of two acids, which he designates as *hexepinic* and *tricipinic* acids.

**Combinations.**—1. With Alkali salts (C. H. Gill, *Chem. Soc. J.* [2], ix. 269). Peligot described a compound of cane-sugar with sodium chloride having the composition  $C^{12}H^{22}O^{11}.NaCl$  (v. 473). Blondran de Carrolas described a similar compound containing  $2C^{12}H^{22}O^{11}.2NaCl.3H^2O$ . Mitscherlich, and afterwards Hochstetter and several other chemists, denied the existence of any saline compounds of cane-sugar. Gill, on the other hand, by leaving a sugar-solution, boiled with excess of common salt, to stand for several months, obtained a few small crystals having the composition  $2C^{12}H^{22}O^{11}.3NaCl.4H^2O$ . A number of similar experiments were made with solutions containing a double molecule of sugar to 1, 2, 3, or 4 mols. of a chloride, bromide, or iodide of an alkali metal.

The potassium salts did not yield compounds of definite composition; some of them, indeed, yielded well-defined crystals containing sugar and salt, but always in variable proportion.

Of the compounds with sodium chloride, that which was obtained from the mixture containing the smallest proportion of salt was to all appearances identical with that described by Peligot. It crystallised from the mixture containing 2 mols. salt to 2 mols. sugar. The crystals, which are prisms with pyramidal summits, do not deliquesce easily, give off all their water of crystallisation when dried for several hours at a temperature of 60° to 70°, and crystallise anhydrous from a solution of 85 p.c. spirit. When a solution in 75 p.c. spirit is mixed with ether, an oily layer separates at the bottom, in which crystals form and continue to grow for 8 to 10 months. These crystals are identical with those of the original compound recrystallised from water, and have the composition  $C^{12}H^{22}O^{11}.NaCl.2H^2O$ . The two other solutions containing

sodium chloride, also gave salts of the same composition. The crystals accidentally obtained at the beginning of the investigation were never reproduced.

Maumens (*Compt. rend.* lxxii. 508) has obtained the compound of sugar with sodium chloride in fine rhombic prisms containing 13.3 p.c. NaCl; it was found by special experiments to contain unmodified cane-sugar.

Sugar solutions, containing *sodium bromide*, gave with difficulty a few crystals, the composition of which,  $C^{12}H^{22}O^{11}.NaBr.1\frac{1}{2}H^2O$ , seemed to indicate the presence of impurities (Gill).

*Sodium iodide* and cane-sugar form extremely fine monoclinic crystals, the same compound,  $2C^{12}H^{22}O^{11}.3NaI.3H^2O$ , being always obtained in whatever proportions its components may be mixed, and crystallising without alteration any number of times from water or aqueous alcohol. In the aqueous solutions the rotatory power of the sugar is unimpaired by the presence of the sodium iodide. The crystals are monoclinic, and have their optic axes in a plane perpendicular to the plane of symmetry (Gill).

*Lithium chloride, bromide, and iodide* do not form definite compounds with cane-sugar. The corresponding *ammonium salts* form very deliquescent crystals containing variable quantities of ammonia. Acetate, nitrate, and phosphate of sodium do not appear to combine with cane-sugar (Gill).

From the composition of the compound with sodium iodide Gill infers that the true molecular weight of cane-sugar is represented by the formula  $C^{12}H^{44}O^{22}$ .

With Lime. According to Horsin-Déon (*Bull. Soc. Chim.* [2], xvii. 155) tribasic sucrate of lime, treated with alcohol, yields the sexbasic sucrate, just as the monobasic sucrate, similarly treated, yields the bibasic compound (v. 473). The mono- and tri-calcic sucraates contain constitutional water; the bi- and sexcalcic compounds do not. The two latter are therefore formed by corresponding reactions:

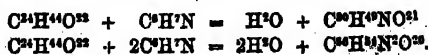


The compound of sugar, lime, and carbonic anhydride, called 'hydrosucro-carbonate of lime,' exhibits, according to Horsin-Déon (*Bull. Soc. Chim.* [2], xv. 22), the following properties: a composition varying with the particular lime sucrate used in its preparation and with the temperature; solubility in sugar-water in presence of lime; decomposition into sucrate and carbonate of lime by sugar-water; capability of formation at all temperatures of experiment and at all densities of the liquid employed. Its varying composition is shown by the following experimental results:

Solution of Lime Sucrate employed	Weight of CO <sup>2</sup> absorbed to 28 pts. by weight of Lime	Experimenter
6 eq. Lime + 1 eq. Sugar	11 parts	Boivin a. Loiseau
5 " " 4 " "	4.4 "	Horsin-Déon
5 " " 3 " "	13.2? "	"
3 " " 2 " "	16.28 "	"
1 " " 1 " "	15.90 "	Dubrunfant
1 " " 1 " "	14.70 "	Horsin-Déon

**Milk-sugar or Lactose**,  $C^{12}H^{22}O^{11}$ , or  $C^{12}H^{44}O^{22}$ . *Oxidation*.—According to Laubenheimer (*Ann. Ch. Pharm.* clxiv. 283), milk-sugar, mixed in aqueous solution with a small quantity of soda, is oxidised by potassium permanganate at ordinary temperatures slowly, but at the boiling heat very quickly and almost completely, to carbon dioxide and water. Attempts to convert it by partial oxidation into malic or isomalic acid were unsuccessful; the filtrate separated after the reaction from manganese dioxide, containing nothing but oxalic acid and uncrystallisable acids.

*Action of Aniline*.—Milk-sugar, heated with twice its weight of aniline, yields, according to circumstances which have not yet been clearly made out, either two nitrogenous products, or only one. The formation of these bodies may be represented by the equations:



Both these bodies are very soluble in water, very sparingly soluble in absolute alcohol, nearly insoluble in pure ether. They reduce alkaline cupric solutions. Bromine, added to their aqueous solutions, disappears immediately (*W. Sächse, Diss. Chem. Ges. Ber.* iv. 834).

**Glucose (dextro) or Dextrose, Lævulose, and Invert-Sugar,  $C^6H^{12}O^6$ .** *Action of Haloids and of certain Chlorides on Dextrose.*—Chlorine does not act on anhydrous dextrose at ordinary temperatures, but at  $80^\circ$  a greenish coloration is produced, and at  $112^\circ$  the mass swells up and becomes carbonised. *Bromine* acts in a similar manner, but the sealed glass tubes in which the action takes place always break at  $80^\circ$ . *Iodine* does not act on dextrose either at  $80^\circ$  or in sunshine. In a stream of *hydrogen chloride*, at  $70^\circ$ , dextrose turns brown, and is converted into a dry black powder.

*Acetyl chloride* acts on dextrose at ordinary temperatures, producing aceto-chlorohydrate,  $C^6H^7(C^2H^3O)ClO^2$ , together with acetic and hydrochloric acids (p. 12).

By the action of chlorine and water, dextrose is converted into gluconic acid,  $C^6H^{12}O^7$  (p. 559).

When dextrose is heated with *baryta-water*, a precipitate is formed; consisting of the barium salt of saccharumic acid,  $C^4H^{10}O^{11}$  (p. 1063), and the liquid filtered therefrom contains the barium salt of glucic or glucinic acid (p. 556).

Lævulose treated with chlorine and water yields glycollic acid (p. 1104).

Invert-sugar treated with water and sodium-amalgam is partly converted into mannito (p. 773).

The action of the electric current on invert-sugar has been examined by H. T. Brown (*Chem. Soc. J.* [2], x. 578). Twenty-four hours after the commencement of the experiment the evolved gas was found to have the following percentage composition :

Carbon dioxide	14.15	Hydrogen	72.80
Carbon monoxide	3.34	Oxygen	9.71

The distillate neutralised with sodium carbonate exhibited the reactions of aldehyde, and the residue in the retort, on further distillation with a little sulphuric acid, yielded a large quantity of acetic and a small quantity of formic acid. The formation of alcohol could not be distinctly proved, but Brown regards it as probable, from the composition of the electrolytic gases. Brister (*Archives Néerlandaises*, 1866, i. 296; *Jahresb.* 1866, 87) obtained, by the electrolysis of a solution of cane-sugar, carbon dioxide and an acid distillate possessing reducing properties, but in which he could not detect either acetic or formic acid.

**Saccharine Substance from Lime-leaves.** A viscid saccharine liquid adhering to the upper side of the diseased leaves of a lime-tree was found by Boussingault (*Ann. Chim. Phys.* [4], xxv. 5) to consist of 55.44 p.c. cane-sugar, 24.75 invert-sugar, and 19.81 dextrin, which is nearly the composition of manna from Sinai (55 cane-sugar, 25 invert-sugar, and 20 dextrin). It melted when exposed to the sun, and fell in drops to the ground, but resumed its viscous state in the shade. Saccharine matter was also found in the healthy leaves of the same tree, but in much smaller quantity, and it was free from dextrin.

On **Bornesite**, see p. 206; **Dambonite**, p. 421; **Dulcete**, p. 440; **Inosite**, p. 669; **Mannite**, p. 773.

**Synanthrose,  $C^{12}H^{22}O^{11}$**  (O. Popp, *Ann. Ch. Pharm.* clvi. 181). This is a variety of sugar which always accompanies inulin in the tuber-bearing Compositæ or Synanthérées; it occurs in all stages of growth, but most abundantly in the ripe bulbs. *Dahlia variabilis* yields it in the greatest quantity and purest state; but the tubers of the Jerusalem artichoke (*Helianthus tuberosus*) may be advantageously used for its preparation. The freshly-expressed juice is treated with lead acetate; the excess of lead removed by sulphuric acid; the filtrate neutralised with magnesium carbonate, lead removed by sulphuric acid; the filtrate neutralised with magnesium carbonate, again filtered, and evaporated to the consistence of an extract; the residue repeatedly exhausted with alcohol so long as the solution possesses rotatory power; the solution evaporated; and the residue exhausted with small quantities of alcohol (not absolute). The resulting solution is treated with animal charcoal, and poured in a thin stream into a mixture of absolute alcohol and ether, and the bulky, white, amorphous precipitate is quickly filtered off, washed with a mixture of alcohol and ether, and dried in a vacuum.

Synanthrose is isomeric with cane-sugar; deliquescent; easily soluble in water and dilute alcohol; difficultly soluble in absolute alcohol, insoluble in ether; optically inactive; does not reduce the solution of copper, or does so only after it has become altered by boiling. Dilute acids convert it into dextrose and lævulose. The rotatory power of inverted synanthrose is  $\alpha = -54.09^\circ$ , and is not influenced by temperature. Its flavour is faint, but not sweet. It is not directly fermentable; yeast acts upon it indeed, but only after splitting it into dextrose and lævulose. At  $140^\circ$ – $145^\circ$  it turns brown, evolves gas, and passes into caramel, glucose and lævulose, the latter apparently optically inactive. Cold caustic alkalis do not turn it brown. Silver concentrated sulphuric acid produces less colour with it than with cane-sugar. Silver

# 1110 SULPHALDEHYDE—SULPHAZOTISED ACIDS.

nitrate in the cold gives a white precipitate, which is reduced on heating, and partially on drying. Copper salts and mercuric chloride give no precipitate, mercuric nitrate gives a bulky white precipitate without reduction. Mercurous nitrate and Millon's solution are at once reduced by it in the cold. Neutral and basic lead acetate give no precipitate; lime and baryta-water give precipitates only on addition of alcohol. Synanthrose does not combine with sodium chloride or other neutral salts; it is decomposed by chlorine and hypochlorites, and gives by dry distillation carbon oxide and dioxide, marsh-gas, acetic acid, and acetone. It forms a hydrate,  $C^{12}H^{22}O^{11} + H^2O$ , the water in which cannot be driven off in the air-bath without decomposition of the synanthrose; it appears to form a similar compound with alcohol. The barium compound,  $C^{12}H^{18}O^{11}Ba^2$ , easily decomposed by carbon dioxide, is difficultly soluble in water, insoluble in alcohol, and easily soluble in dilute acids. The lead compound,  $C^{12}H^{18}O^{11}Pb^2$ , is more stable than the barium compound, and dissolves easily in acetic acid or lead acetate.

Synanthrose interferes with the precipitation of copper, iron, and chromium oxides. Ferric oxide, freshly precipitated in the cold, dissolves in solution of synanthrose, and by evaporation is reduced to magnetic oxide, glucose being also formed. By treatment with chromic acid or lead dioxide, it yields formic acid. With hot dilute nitric acid, it gives saccharic and oxalic acids.

When synanthrose is treated with a cold mixture of 1 pt. concentrated nitric acid and 2-2½ pts. sulphuric acid, an explosive nitro-compound is formed, soluble in alcohol, less soluble in water than synanthrose itself. By acetic, butyric, and tartaric acids at 100°, synanthrose is converted into glucose. The prolonged action of sulphuric or hydrochloric acid produces glucic acid and finally humus compounds.

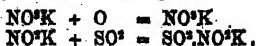
**SULPHALDEHYDE.** See ALDEHYDE (p. 37).

**SULPHAMIDOBENZOIC ACIDS.** See SULPHOBENZOIC ACIDS (p. 1113).

**SULPHAMMONIC ACIDS.** See SULPHAZOTISED ACIDS (*infra*).

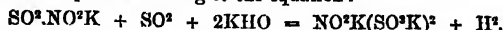
**SULPHANILIC ACID,**  $C^6H^5NSO^2 = C^6H^4 \begin{Bmatrix} NH^2 \\ SO^2H \end{Bmatrix}$ . This acid, formed from aniline and sulphuric acid, is converted by nitrous acid into diazosulphanilic acid,  $C^6H^4 \begin{Bmatrix} N=N \\ SO^2 \end{Bmatrix}$ , which, when heated with water, yields a phenol-sulphonic acid,  $C^6H^4 \begin{Bmatrix} OH \\ SO^2H \end{Bmatrix}$ , convertible by fusion with potash into resorcin. The same diazosulphanilic acid, heated with hydrobromic acid, yields a bromo-benzenesulphonic acid,  $C^6H^4 \begin{Bmatrix} Br \\ SO^2H \end{Bmatrix}$ , also convertible by fusion with potash into pure resorcin. According to the view now entertained of the composition of resorcin, these facts indicate that the sulphanilic acid prepared by direct combination is a meta-compound (1 : 3). On the other hand, when the bromobenzenesulphonic acid obtained as just described, is distilled with potash, it yields dicyanobenzene,  $C^6H^4(ON)^2$ , which, by boiling with potash, is converted into terephthalic acid, which is a para-compound. Hence, it appears probable that the conversion of the bromobenzenesulphonic acid into dicyanobenzene is accompanied by a molecular transposition (see BENZENE, p. 136).

**SULPHAZOTISED ACIDS.** (Claus, *Deut. Chem. Ges. Ber.* iv. 186, 221 and 504; *Ann. Ch. Pharm.* clviii. 52, 104; *Bull. Soc. Chim.* [2], xv. 179; xvi. 76; *Chem. Soc. J.* [2], ix. 307, 659). These acids, of which the sulphammonic acids (1st Suppl. 1047) form a particular group, are produced by the action of sulphurous acid on potassium nitrite. Their formation depends on a simple reduction of the nitrous acid, but with this peculiarity, that before the reduction has proceeded so far as the formation of ammonia, the more or less reduced product from the nitrous acid enters into combination with the group  $SO^2K$ , resulting from oxidation of the sulphurous acid. Thus the sulphoxazic acids are the stepping stones to the sulphammonic acids, the former being, in fact, convertible into the latter by further reduction with sulphurous acid. The formation of the sulphazotised acids is, however, partly assisted by the tendency of trivalent nitrogen to pass into the quinquivalent condition. Just as potassium nitrite can pass into nitrate by taking up an atom of oxygen, so likewise has it a tendency to take up the bivalent group  $SO^2$ :



The compound  $SO^2NO^K$ , which, in the ordinary method of preparing these acids (p. 1111), is decomposed as fast as it forms, may, in fact, be isolated by acting on potas-

sium nitrite with an alcoholic solution of sulphurous acid, the salt so formed, immediately separating out and being thereby withdrawn from the further action of the sulphurous acid. On again subjecting this salt to the action of sulphurous acid, which, perhaps, takes place according to the equation :



other sulphazotised acids are produced by the action of the nascent hydrogen, either on the newly formed salt, or on the compound which precedes it, or finally on the potassium nitrite, with or without the simultaneous action of fresh sulphurous acid.

The usual mode of preparing the sulphazotised acids is to pass sulphurous acid into an alkaline solution of potassium nitrite, the products thus formed varying in composition accordingly as the solution is cooled or not during the passage of the gas.

All these acids are sulphonic acids, containing either trivalent or quinquivalent nitrogen, which may also be united with oxygen or with hydrogen. Claus accordingly distinguishes three groups :

1. *Sulphammonic compounds*, all containing quinquivalent nitrogen, which, besides the sulphonic group  $\text{SO}^{\cdot}\text{K}$ , is combined only with hydrogen. These compounds, when ignited with soda-lime, give off the whole of their nitrogen as ammonia.

2. *Sulphoxyazic compounds*, likewise containing only quinquivalent nitrogen, which, however, is united with oxygen as well as with hydrogen. When heated with soda-lime, they give off only a part of their nitrogen in the form of ammonia.

3. *Sulphamic compounds* containing only trivalent nitrogen.

Of these three classes, the following compounds have been examined :

(1). Sulphammonates :

$\text{N}^{\cdot}\text{H}(\text{SO}^{\cdot}\text{K})^4$  Tetrasulphammonate of potassium

$\text{N}^{\cdot}\text{H}^2(\text{SO}^{\cdot}\text{K})^3$  Trisulphammonate of potassium

$\text{N}^{\cdot}\text{H}^3(\text{SO}^{\cdot}\text{K})^2$  Disulphammonate of potassium.

The monosulphammonate,  $\text{N}^{\cdot}\text{H}^4(\text{SO}^{\cdot}\text{K})$ , has not been obtained; it would be isomeric, or perhaps even identical, with ammonio-potassic sulphite,  $\text{SO} \begin{Bmatrix} \text{OK} \\ \text{ONH}^4 \end{Bmatrix}$ .

(2). Sulphoxyazates :

$\text{ON}^{\cdot}\text{H}(\text{SO}^{\cdot}\text{K})^2$ . Disulphoxyazate of potassium: hard, transparent, shining crystals sparingly soluble in cold, easily in hot water; decomposes when heated above  $60^{\circ}$ .

$\text{ON}^{\cdot}(\text{SO}^{\cdot}\text{K})^3$ . Trisulphoxyazate of potassium: shining, transparent, rhombic plates, moderately stable.

$\text{HN}^{\cdot} - \text{N}^{\cdot}\text{O}$   
 $\begin{array}{c} ||| \quad | \\ (\text{SO}^{\cdot}\text{K})^3\text{OK} \quad | \\ | \quad | \end{array}$   
 $(\text{SO}^{\cdot}\text{K})^3\text{OK}(\text{SO}^{\cdot}\text{K})$ . Sulphazotate of potassium: colourless, translucent, rhombic plates, which may be heated to  $150^{\circ}$ .

$\text{N}^{\cdot} - \text{NO}$   
 $\begin{array}{c} \diagup \quad \diagdown \\ | \quad | \\ (\text{SO}^{\cdot}\text{K})^3 \quad | \\ | \quad | \end{array}$   
 $(\text{SO}^{\cdot}\text{K})^3(\text{SO}^{\cdot}\text{K})$ . Oxysulphazotate of potassium: needles of a deep yellow colour; very unstable.

(3). Sulphamates :

$\text{NH}(\text{OH})(\text{SO}^{\cdot}\text{K})$ . Sulphhydroxylamate of potassium.

$\text{NH}(\text{OH})(\text{SO}^{\cdot}\text{H})$ . Sulphhydroxylamic acid.

The aqueous solution of this acid may be boiled for a short time without decomposition.

Instead of the names above given to the compounds of the first and second groups, the following, in which the prefix 'azo' denotes nothing more than a nitrogen-compound, are proposed by Michaelis (*Jahresb. f. Chem.* 1872, 234), as more characteristic:—

$\text{NH}(\text{SO}^{\cdot}\text{K})^4$	Hydrazotetrasulphonate
$\text{NH}^2(\text{SO}^{\cdot}\text{K})^3$	Hydrazotrisulphonate, &c. &c.
$\text{ONH}(\text{SO}^{\cdot}\text{K})^3$	Hydrazoxydisulphonate
$\text{ON}(\text{SO}^{\cdot}\text{K})^4$	Azotetrasulphonate
$\text{N}^{\cdot}\text{HO}^{\cdot}\text{K}(\text{SO}^{\cdot}\text{K})^4$	Diazohydroxypotassiotetrasulphonate
$\text{N}^{\cdot}\text{O}^{\cdot}(\text{SO}^{\cdot}\text{K})^4$	Diazotetrasulphonate.

**SULPHETHERS OF ETHYLENE.** See ETHYLENE (p. 491).

**SULPHIDES OF HYDROGEN.** *Monosulphide: Sulphydric acid: Sulphuretted Hydrogen.*—On the formation and preparation of this gas, and the decomposition of its aqueous solution, see p. 661. The gas is commonly said to require a red heat to decompose it. According to J. Myers, however (*Ann. Ch. Pharm.* cliz. 124), the decomposition begins at 400°, and proceeds rapidly at the boiling point of sulphur.

*Basicity of Sulphydric acid.*—J. Thomsen (*Pogg. Ann.* cxxxix. 193; *Jahresb.* 1870, 120) regards sulphydric acid as a monobasic acid,  $\text{H.SH}$ ; first, because the heat developed on adding to it successive quantities of sodium hydrate does not increase after the addition of 1 mol.  $\text{NaHO}$  (1st *Suppl.* 683); secondly, because the second atom of hydrogen cannot be replaced by sodium acting on the aqueous solution. For similar reasons also he regards water as a monobasic acid,  $\text{H.OH}$ . According to this view, the so-called neutral sulphides, such as  $\text{Na}^2\text{S}$ —like the corresponding anhydrous oxides, *e. g.*,  $\text{Na}^2\text{O}$ —cannot exist in aqueous solution, and the soluble normal salts of sulphydric acid must be regarded as  $\text{Na.SH}$ ,  $\text{Ba}(\text{SH})^2$ ,  $\text{Mg}(\text{SH})^2$ , &c. Kolbe (*J. pr. Chem.* [2], iv. 412) objects to this view, on the ground that, if an aqueous solution of sodium sulphide contains nothing but the sulphydrate and hydrate of sodium, it should, when treated with potassium ethylsulphate, yield nothing but mercaptan, whereas it always yields in addition ethyl sulphide,  $(\text{C}^2\text{H}^5)^2\text{S}$ , the quantity of which is greater as the solution of sodium sulphide is more concentrated. Kolbe therefore concludes that the resolution of the sodium sulphide into sulphydrate and hydrate is complete only in very dilute solutions (such as those used by Thomsen), and very partial in concentrated solutions, and therefore that Thomsen's view of the monobasicity of sulphydric acid is erroneous. Thomsen (*ibid.* v. 247) agrees with Kolbe that the decomposition of metallic sulphides by water is more complete in dilute than in concentrated solutions, but regards his inference from the formation of ethyl sulphide in the reaction just mentioned as inconclusive, inasmuch as the reaction is complicated by the presence of sodium hydrate.

*Persulphide.*—The composition of this compound is still a matter of doubt. Hofmann, in 1868, obtained a crystalline compound of hydrogen persulphide with strychnine, having the composition  $\text{C}^{21}\text{H}^{22}\text{N}^2\text{O}^2.\text{H}^2\text{S}^2$ , and hence inferred that the persulphide itself is  $\text{H}^2\text{S}^2$ ; he did not, however, succeed in isolating it. Similar results have recently been obtained by W. Ramsay (*Chem. Soc. J.* [2], xii. 857), who likewise did not succeed in isolating the persulphide, or in obtaining it of definite composition by any other process. Drochsel (*J. pr. Chem.* [2], iv. 20; *Jahresb.* 1871, 211), on the other hand, regards the persulphide as a pentasulphide,  $\text{H}^2\text{S}^5$ , analogous to  $\text{K}^2\text{S}^5$ , because it may be formed from the latter (?) by decomposition with acids), and reconverted into it by the action of alcoholic potassium sulphydrate:



Hydrogen persulphide is an almost colourless oil of sp. gr. 1.7342, somewhat soluble in alcohol, insoluble in benzene and chloroform. It dissolves phosphorus and iodine, but the solutions gradually decompose, giving off sulphydric acid, and forming phosphorus iodide or hydriodic acid respectively. Chlorine passed through it forms hydrochloric acid and sulphur chloride,  $\text{S}^2\text{Cl}^2$ . Bromine acts in a similar manner. *Sulphurous anhydride* has but very little action on it. *Ammonia*, either gaseous or in solution, decomposes it instantly, leaving sulphur in a peculiarly brittle blistered state. On *organic bodies* the persulphide exerts a more powerful reducing action than the monosulphide (Ramsay).

**SULPHIDES, METALLIC.** *Formation by the action of Alkaline Sulphides on Metals* (Priwosnik, *Ann. Ch. Pharm.* clxiv. 46).—Pure copper immersed in yellow ammonium sulphide to which a considerable quantity of sulphur has been added, becomes covered with a crust of cupric sulphide,  $\text{CuS}$ , blue-black on the outer, brown-black on the inner surface, easily separating from the metal and continually renewed. If the action be allowed to go on for several days, the monosulphide changes into black cuprous sulphide,  $\text{Cu}^2\text{S}$ , the supernatant transparent and colourless liquid then consisting of ammonium monosulphide. The yellow solutions of potassium and sodium sulphide likewise give up their excess of sulphur to copper, and become colourless. This reaction affords an easy method of forming the alkaline monosulphides; a little copper, however, is apt to be taken up. *Sodium thiosulphate* is also decomposed at the boiling heat by copper, especially in the finely divided state; thus:



*Silver*, as is well known, is blackened by alkaline sulphides. Chemically pure silver immersed in yellow ammonium sulphide becomes coated with a very closely adhering lead-gray film, which becomes thicker on prolonged immersion, and after about six



weeks forms a crystalline crust of the monosulphide  $\text{Ag}_2\text{S}$ , which easily splits off on bending the plate.

*Tin*, under similar circumstances, likewise unites with sulphur, but does not form a crust, because the resulting sulphide dissolves in the sulphide of alkali-metal.

*Nickel* behaves exactly like tin, imparting to yellow ammonium sulphide a dark colour which passes through brown into black. This reaction serves to distinguish nickel from cobalt (p. 849).

An *iron wire*, a millimeter thick, immersed in ammonium polysulphide, gradually became covered with an extremely thin velvet-black film, which was easily rubbed off.

**Formation by the action of Thiosulphates.**—Metallic oxides or salts, heated with anhydrous sodium thiosulphate, are converted into sulphides, exhibiting, for the most part, the same colours as when they are formed by precipitation with hydrogen sulphide. Manganic oxide, however, is converted into green oxysulphide,  $\text{Mn}^2\text{OS}$ , and stannic oxide into brown stannous sulphide (Landauer, *Zeitschr. Ann. Chem.* 1872, 427).

**Action of Iodine on Insoluble Sulphides.**—A mixture of zinc sulphide and dry iodine immediately becomes hot, with separation of sulphur, and formation of zinc iodide; to complete the decomposition, however, the mixture must be heated to  $200^\circ$  in sealed tubes. Zinc sulphide suspended in water is acted on in the same manner by iodine, either dry, or dissolved in water or alcohol, excepting that a small quantity of zinc sulphate (15 pts. to 1000 of the zinc sulphide) is produced at the same time. The sulphate is also formed in small quantity, together with zinc iodide and free sulphur, in the action of dry zinc sulphide on solutions of iodine in ether or chloroform; no sulphate, however, is formed in the action of zinc sulphide on iodine dissolved in carbon sulphide. Native *zinc blende* is attacked by iodine only at high temperatures, best at  $200^\circ$ ; in presence of water a little sulphate is likewise formed. The formation of the sulphate appears to be due, not to the absorption of oxygen from the air by the sulphide, but to the decomposition of water, with formation of hydriodic acid. Similar results are obtained by the action of iodine on the sulphides of manganese, cadmium, iron, nickel, cobalt, tin, antimony, arsenic, bismuth, lead, mercury, silver, and platinum (Filhol a. Mellies, *Ann. Chim. Phys.* [4], xxii. 58).

On the electric conductivity and electromotive power of metallic sulphides, see ELECTRICITY (p. 446); also *Chem. News*. xxiii. 161.

**SULPHINIC ACIDS.** Organic sulphur-acids formed on the type  $\text{R}-\text{SOOH}$ , R denoting a monatomic alcohol radicle; they contain 1 at. oxygen less than the sulphonic acids.

**SULPHOBENZENIC or SULPHOBENZOLIC ACIDS.** Syn. with BENZENESULPHONIC ACIDS (p. 152).

**SULPHOBENZOIC ACID**,  $\text{C}_6\text{H}_5\text{O}_2\text{SO} = \text{C}_6\text{H}_5 \begin{Bmatrix} \text{SO}^+\text{H} \\ \text{COOH} \end{Bmatrix}$ . **Formation.**—Benzoyl chloride, treated with sulphuric acid, is converted into benzoyl-sulphuric acid,  $\text{SO}_2 \begin{Bmatrix} \text{OH} \\ \text{O}(\text{C}_6\text{H}_5\text{O}) \end{Bmatrix}$ , which on keeping, and still more on heating, changes into the isomeric sulphobenzoic acid, identical with that which is prepared by the action of sulphuric acid on benzoic acid (Oppenheim, *Deut. Chem. Ges. Ber.* iii. 735).

**Action of Potassium Hydrate.**—Crude sulphobenzoic acid fused with potash is converted into a mixture of oxybenzoic and paraoxybenzoic acids. These two acids cannot be separated by fractional crystallisation; but an approximate separation may be effected by adding barium hydrate to the mixed solution of their barium salts, whereby a basic barium paraoxybenzoate is formed, which is but slightly soluble in water; oxybenzoic acid does not form a basic barium salt under these circumstances. The formation of these two acids shows that crude sulphobenzoic acid is a mixture of meta- and parasulphobenzoic acid.

**Acid Parasulphobenzate of Barium**,  $(\text{C}_6\text{H}_5\text{SO})_2\text{Ba} + 3\text{H}_2\text{O}$ , is sparingly soluble in hot water (much less than the meta-salt), nearly insoluble in cold water; when pure it crystallises from the hot solution in flat needles, which fill the containing vessel from top to bottom. The neutral potassium salt is very easily soluble both in hot and in cold water, and crystallises in needles. When fused with potash it yields perfectly pure paraoxybenzoic acid, whereas the potassium salt prepared from acid metasulphobenzate of barium yields by fusion with potash nothing but oxybenzoic acid (Ira Remsen, *Zeitschr. f. Chem.* [2], vii. 81, 199).

**Amidosulphobenzic Acids**,  $\text{C}_6\text{H}_4(\text{NH}_2)\text{O}_2\text{SO}^+\text{H}$  (Griess, *J. pr. Chem.* [2], v. 244). Two isomeric acids having this composition are obtained by heating a solution of amidobenzoic acid in fuming sulphuric acid to  $170^\circ$ , dissolving the resulting dirty-white crystalline mass in a large quantity of boiling water, neutralising with barium

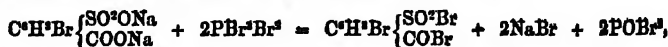
carbonate, and evaporating the solution to the crystallising point. It then deposits small, well-defined, six-sided tables or prisms consisting of the barium salt of one of the sulpho-acids, and the mother-liquor, on further evaporation, yields thick white needles or small prisms of the barium salt of the other acid. This last-mentioned barium salt has the composition  $C^6H^4(NH^2)O^2.SO^2Ba + 3H^2O$ . On supersaturating its hot aqueous solution with hydrochloric acid, the free acid separates almost completely on cooling, in soft, white, six-sided laminae, or in nodules, very slightly soluble in boiling water, almost insoluble in alcohol and ether. It is anhydrous, has a sour taste, and is bibasic. Heated with strong nitric acid it is converted, with separation of sulphuric acid, into an easily soluble nitro-acid.

The barium salt of the other amidosulphobenzoic acid has, when air-dried, the composition  $C^6H^4(NH^2)O^2.SO^2Ba + 2H^2O$ . By converting it into an ammonium salt and precipitating the solution of the latter with hydrochloric acid, the free acid is obtained in narrow four-sided laminae, which are easily soluble in hot water, and have, when air-dried, the composition  $C^6H^4(NH^2)O^2.SO^2H + H^2O$ .

These amidated sulpho-acids are likewise produced, with separation of carbon dioxide and ammonia, by the action of fuming sulphuric acid on amidobenzoic cyanide (1st Suppl. 317). The amidosulphobenzoic acid, which Limpriecht and v. Usler obtained by reducing nitrosulphobenzoic acid with ammonium sulphide (v. 488), is probably a third modification.

**Bromosulphobenzoic Acid**,  $C^6H^3BrSO^2 = C^6H^3Br \begin{Bmatrix} CO^2H \\ SO^2H \end{Bmatrix}$  (Roeters van Lennep, *Zeitschr. f. Chem.* [2], vii. 67). This acid is prepared by heating bromobenzoic acid (m. p. 152°) with sulphuric anhydride till the mixture nearly ceases to give off vapour of the anhydride, then pouring it into water, separating the solution from unaltered bromobenzoic acid, boiling the filtrate with lead carbonate, and decomposing the resulting lead salt with hydrogen sulphide. It crystallises in small, delicate, deliquescent needles. Its salts, especially the neutral salts, crystallise very badly, forming dense masses which retain moisture, so that it is difficult to determine their amount of water of crystallisation. The *neutral sodium salt* forms clusters of small needles. The *acid sodium salt*,  $C^6H^3Br.CO^2H.SO^2Na$ , separates from the solution of the neutral salt in hydrochloric acid, and may be obtained in well-defined needles by recrystallisation from alcohol. The *neutral barium salt*,  $C^6H^3Br.CO^2.SO^2Ba + 2\frac{1}{2}H^2O$ , crystallises in tufts of needles easily soluble in water and in rather strong boiling alcohol. The *acid barium salt*,  $(C^6H^3Br.CO^2H.SO^2)^2Ba + H^2O$ , is formed when the neutral salt is crystallised from hydrochloric acid, and may be obtained in very small needles by recrystallisation from alcohol. The *calcium salt*,  $C^6H^3Br.CO^2.SO^2Ca + 1\frac{1}{2}H^2O$ , obtained by boiling the crude acid with slaked lime or chalk, dissolves easily in water, sparingly in alcohol either cold or hot, and crystallises easily from hot alcohol in needles. The *magnesium salt* forms small needles easily soluble in water, sparingly in alcohol. The *copper salt*,  $C^6H^3Br.CO^2.SO^2Cu$ , forms nodular groups of green, sparingly soluble needles. The *lead salt*, prepared as above described, also forms nodular groups of needles sparingly soluble in water and in alcohol. The *silver salt*,  $C^6H^3Br.CO^2Ag.SO^2Ag$ , crystallises in white, slightly soluble needles.

*Action of Phosphorus Pentabromide on Sodium Bromosulphobenzoate*.—This reaction, which probably takes place according to the equation:



yielded an oil, which was washed with water to remove sodium bromide, and then boiled with water to convert the group COBr into the group COOH. Heat partly decomposed the resinous product, thus:



It was now dissolved in soda-solution, filtered from the insoluble portion, and precipitated by hydrochloric acid, when it yielded a very small quantity of an acid. Neither this acid, nor its sodium salt, could be obtained in a distinctly crystalline state from their solutions in alcohol or water, but one or two sublimations gave the acid in slender glistening needles melting at 182°–184°.

**Thiobenzoic Acid**,  $C^6H^4 \begin{Bmatrix} SH \\ COOH \end{Bmatrix}$  (Hübner a. Upmann, *Zeitschr. f. Chem.* [2], vi. 291; van Leunep, *loc. cit.*) This acid, the sulphur-analogue of oxybenzoic acid, is prepared: 1. By heating sodium sulphobenzoate with twice its weight of phosphorus pentachloride, and treating the resulting sulphobenzoic chloride,  $C^6H^4.SO^2Cl.COCl$ , with tin and hydrochloric acid. The crystalline mass which separates is washed with hydrochloric acid, dissolved in ammonia, precipitated by an acid,

# SULPHOCAMPHORIC ACID—SULPHOCARBAMIDE. 1115

and recrystallised from alcohol containing hydrochloric acid (Hübner a. Upmann). 2. By reducing bromothiohydrobenzoic acid (*infra*) with sodium-amalgam and water, precipitating with dilute sulphuric acid and recrystallising from water (van Lennep).

Thiohydrobenzoic acid is nearly insoluble in water, sparingly soluble in alcohol, and crystallises from the latter in needles having a faint yellowish colour, but may be obtained white by solution in ammonia and precipitation by hydrochloric acid. It melts at  $242^{\circ}$ – $244^{\circ}$ . The ammonium salt,  $C^6H^4(SH)CO^2NH^4 + H^2O$ , is soluble in water and alcohol, and separates, on evaporation, as a granulo-crystalline mass. The barium salt,  $[C^6H^4(SH)CO^2]^2Ba + 2\frac{1}{2}H^2O$ , is obtained by precipitating a boiling, very dilute solution of the ammonium salt with barium chloride, in small white prismatic needles. The calcium salt,  $[C^6H^4(SH)CO^2]^2Ca + 3H^2O$ , is a light yellow granulo-crystalline precipitate. The zinc and lead salts are likewise obtained by precipitation (Hübner a. Upmann).

**Bromothiohydrobenzoic acid**,  $C^6H^4Br \begin{Bmatrix} SH \\ CO^2H \end{Bmatrix}$ , is prepared from bromosulphobenzoic acid in the same manner as thiohydrobenzoic acid from sulphobenzoic acid. The mass, separated by the action of tin and hydrochloric acid, dissolves for the most part in alcohol, and, on evaporating the solution, the bromothiohydrobenzoic acid separates in small colourless needles melting at  $256^{\circ}$  (Upmann), at  $242^{\circ}$ – $243^{\circ}$  (van Lennep). It is insoluble in water, but dissolves easily in alcohol. By the action of water and sodium-amalgam it is converted into thiohydrobenzoic acid. The zinc salt,  $(C^6H^4Br.SHCOO)^2Zn$ , is precipitated on adding zinc sulphate to a solution of the ammonium salt; it is insoluble in water. The lead salt,  $(C^6H^4Br.SHCOO)^2Pb$ , is a white precipitate, insoluble in water, prepared by adding lead acetate to a solution of the ammonium salt. The barium salt,  $(C^6H^4Br.SHCOO)^2Ba$ , forms a white precipitate, obtained by adding barium chloride to the ammonium salt. It is somewhat soluble in boiling water, and, on evaporation, separates in microscopic crystals. The calcium salt, like the barium salt, is a white precipitate. The sodium salt, after treatment with iodine, yields an acid having a melting point of  $130^{\circ}$ . Its lead and zinc salts,  $(C^6H^4Br.S.CO^2)^2Zn$ , are white precipitates, insoluble in water (van Lennep).

**SULPHOCAMPHORIC ACID**,  $C^6H^{10}SO^4$ . This acid and its salts are inactive to polarised light, although they are derived from the anhydride of camphoric acid, which has a rotatory power of about  $-7^{\circ}$  (Kachler, *Ann. Ch. Pharm.* clxii. 259).

**SULPHOCARBAMIDE**. Sulphurea,  $CS \begin{Bmatrix} NH^2 \\ NH^2 \end{Bmatrix}$ .—This body, heated in a sealed vessel with nearly anhydrous aldehyde, forms the compound  $CS \begin{Bmatrix} N.C^2H^4 \\ NH^2 \end{Bmatrix}$ , which dissolves sparingly in ether and cold alcohol, more readily in hot alcohol, not at all in cold water, and is decomposed, by boiling with water, into aldehyde, sulphocarbamide, and a small quantity of ammonium sulphocyanate. Dilute acids act upon it in the same way (J. E. Reynolds, *Chem. News*, xxiv. 87).

The analogous oxygen-compound,  $CO \begin{Bmatrix} N.C^2H^4 \\ NH^2 \end{Bmatrix}$ , described by Schiff (*Ann. Ch. Pharm.* cli. 206), is formed by the action of aldehyde on carbamide (urea).

**Diphenylsulphocarbamide**,  $N^2(CS)(C^6H^5)^2H^2$ .—On the action of an alcoholic solution of nitrous ether on this compound, see p. 436.

**Oxybenzoylsulphocarbamide**,  $C^6H^4N^2O^2S = N^2 \begin{Bmatrix} CS \\ C^6H^4O^2 \\ H^2 \end{Bmatrix}$ .—This compound is formed by heating amidobenzoic sulphate on the water-bath with a quantity of water not sufficient to dissolve it completely, and adding an equivalent quantity of potassium sulphocyanate in crystals, whereupon the whole dissolves in the form of easily soluble amidobenzoic sulphocyanate,  $C^6H^4NO^2.CHNS$ . By very strong concentration a crystalline deposit is obtained, consisting chiefly of potassium sulphate; and, on evaporating to dryness on the water-bath, exhausting with alcohol, evaporating the alcoholic solution to dryness, and crystallising the residue several times from boiling water, oxybenzoylsulphocarbamide, resulting from molecular transformation of the amidobenzoic sulphocyanate, is obtained in the pure state.

Oxybenzoylsulphocarbamide is nearly insoluble in cold water and alcohol, but dissolves readily in both these liquids at the boiling heat. The hot aqueous solution forms white precipitates with the chlorides of barium and calcium and the nitrates of silver and lead, and a brown-red precipitate with ferric chloride. It is desulphurised by silver or lead nitrate in presence of alkalis, also by mercuric oxide and silver oxide, being probably converted into the carbamide of oxybenzoic acid (Arzruni, *Deut. Chem. Ges. Ber.* iv. 406).

*Pseudotolyl-sulphocarbamide*,  $C^6H^4N^2S = CS(NH.C^6H^3)$ , is formed by heating pseudotoluidine on the water-bath, with an alcoholic solution of carbon sulphide, as long as hydrogen sulphide continues to escape, and separates out, partly during the reaction, partly on cooling. This compound, when recrystallised from alcohol, forms white woolly needles extremely soluble in alcohol and ether, melting at  $165^\circ$  (uncorr.) (E. Gerard, *Deut. Chem. Ges. Ber.* iv. 985).

**SULPHOCARBIMIDES.** See SULPHOCYANIC ETHERS (p. 1117).

**SULPHOCARBONYL CHLORIDE**,  $CSOCl^2$ . See CARBON SULPHOCHLORIDES (p. 266).

**SULPHOCINNAMIC ACID**,  $C^6H^5SO^2$ . Cinnamic acid treated with strong sulphuric acid yields two isomeric sulpho-acids. The para-acid,  $C^6H^5SO^2 + 5H^2O$ , crystallises in large monoclinic prisms; its barium salt,  $(C^6H^5SO^2)^2Ba + 3H^2O$ , forms long, sparingly soluble needles. By fusion with potash the acid is converted into paraoxybenzoic acid. The isomeric acid forms indistinct crystals; its barium salt,  $(C^6H^5SO^2)^2Ba + 1\frac{1}{2}H^2O$ , crystallises in nodules. The salts of this latter acid are more soluble than the corresponding para-salts. By fusion with potash it appears to yield oxybenzoic acid.

**SULPHOCOUMARILIC ACID**,  $C^6H^4O^2SO^2$  (Perkin, *Chem. Soc. J.* [2], ix. 49). This acid is formed by digesting 1 pt. of coumarin with 5 pts. of fuming sulphuric acid on the water-bath for an hour or two. The product dissolves perfectly in water, and the solution neutralised with barium carbonate yields, besides barium sulphate, the soluble barium salt of sulphocoumarilic acid; and by decomposing this salt with the exact quantity of sulphuric acid required, then filtering, and evaporating, first over the water-bath, afterwards in a vacuum, sulphocoumarilic acid is obtained in easily soluble needles having the composition  $C^6H^4O^2SO^2H + 2H^2O$ . The ammonium salt crystallises in silky, easily soluble needles. The sodium salt forms transparent rhombic crystals nearly insoluble in alcohol. The potassium salt crystallises in flat prisms. The barium salt,  $(C^6H^4O^2SO^2)^2Ba + 5H^2O$ , and the strontium salt,  $(C^6H^4O^2SO^2)^2Sr + H^2O$ , crystallise well.

**Disulphocoumarilic Acid**,  $C^6H^4O^2(SO^2H)^2$ . A mixture of about 8 pts. fuming sulphuric acid and 1 pt. coumarin, heated to  $150^\circ$ – $160^\circ$ , for an hour or two, yields a product containing sulphocoumarilic and disulphocoumarilic acids; and on neutralising this mixture with barium carbonate, evaporating to dryness, and treating the residue with warm water, barium sulphocoumarilate is dissolved, while the less soluble disulphocoumarilate remains behind, and may be purified by recrystallisation from warm water. This salt,  $C^6H^4O^2(SO^2)^2Ba + H^2O$ , forms a white crystalline powder nearly insoluble in cold, and but slightly soluble in hot water (Perkin).

**SULPHOCYANACRINYL** or **ACRINYL SULPHOCYANATE**,  $C^6H^4NSO$ . A product of the decomposition of sinalbin. See MUSTARD (p. 832).

**SULPHOCYANATES.** Synthesis of *Ammonium Sulphocyanate*.—According to Berthelot (*Jahresb. f. Chem.* 1868, 160), carbon sulphide is not acted upon by gaseous ammonia at ordinary temperatures, even after several hours' contact. Heys van Zouteveen, on the other hand (*Archives Néerlandaises*, v. 240), finds that when dry ammonia gas is passed into carbon sulphide, a brick-red precipitate is formed, the aqueous solution of which, when evaporated over a Bunsen flame to half its bulk, becomes decolorised, gives off vapours of carbon sulphide and ammonium sulphide, and deposits a small quantity of sulphur, leaving a solution of ammonium sulphocyanate, as shown by its reaction with ferric salts.

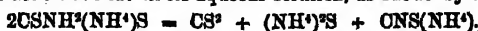
The first stage of the reaction appears to be:



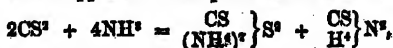
analogous to—



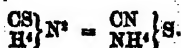
(1st *Suppl.* 408), the ammonium sulphocarbamate thus formed being subsequently decomposed by the action of heat on its aqueous solution, as shown by the equation:



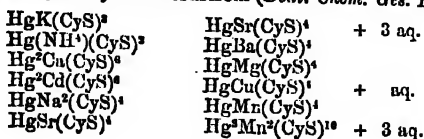
The process may also be supposed to take place as follows: first—



and then, on boiling the mixture:



**Mercurio Sulphocyanate.**—The following double salts of this compound have been prepared and analysed by Th. Nordström (*Deut. Chem. Ges. Ber.* iv. 989).



**Potassium Isosulphocyanate**,  $\text{N} \left\{ \begin{smallmatrix} \text{CS} \\ \text{K} \end{smallmatrix} \right.$ .—This salt is obtained by the action of alcoholic potash on persulphocyanic acid, as a yellow granular mass, which may be decolorised by boiling with very strong alcohol, and freed from adhering water by exposure over oil of vitriol. It dissolves easily in water, is nearly insoluble in strong alcohol, but soluble in very weak spirit. By leaving the aqueous solution for some time in a vacuum over sulphuric acid, it is obtained in crystals having the composition  $2\text{KNCS} + \text{H}^{\text{o}}\text{O}$ . The following reactions distinguish the isosulphocyanate from the ordinary sulphocyanate:

	Sulphocyanate	Isosulphocyanate
Silver nitrate .	White precipitate, soluble in ammonia .	Light yellow precipitate, scarcely soluble in ammonia
Basic acetate of lead	White voluminous precipitate . . .	Yellow precipitate
Copper sulphate	Black pulverulent precipitate . . .	Greenish-yellow precipitate
Cobalt sulphate .	Rose-red coloration . . .	Brownish-green precipitate
Nickel sulphate .	Greenish coloration . . .	Reddish precipitate
Cadmium sulphate	. . . . .	White precipitate
Zinc chloride .	No reaction . . .	Deep yellow, voluminous precipitate
Mercuric chloride	. . . . .	White voluminous precipitate
Mercurous nitrate .	Grey precipitate . . .	Black precipitate

Ferric chloride gives, with neutral solutions of the isosulphocyanate, a brown coloration, which disappears on adding excess of the iron solution; a yellow pulverulent body separates from the liquid on standing.

Potassium isosulphocyanate may be partially converted into sulphocyanate by repeated evaporation of its aqueous or weak alcoholic solution on the water-bath, and completely by fusion.

A smell, similar to that of mustard-oil, is observed on leaving ethyl iodide in contact with isosulphocyanate of potassium or silver (*Fleischer, Deut. Chem. Ges. Ber.* iv. 190).

**Sulphocyanic Ethers.** *Allyl Isosulphocyanate* or *Sulphocarbimide*.

**Volatile Oil of Mustard.**  $\text{N} \left\{ \begin{smallmatrix} (\text{CS})^{\text{a}} \\ \text{C}^{\text{a}}\text{H}^{\text{a}} \end{smallmatrix} \right.$ . According to Vollrath (*Arch. Pharm.* [2], cxlviii. 156), this oil forms an essential constituent of the root of mignonette. It mixes with strong sulphuric acid without coloration. On adding 3 pts. of strong sulphuric acid drop by drop to 1 pt. of mustard oil, both being cooled by ice, decomposition sets in, attended with evolution of sulphurous acid and carbon oxy-sulphide (*Flückiger, Arch. Pharm.* [2], cxlv. 214; *Chem. Soc. J.* [2], ix. 835).

Mustard-oil unites directly with *acid potassium sulphite*, when boiled with it in concentrated solution, forming the compound  $\text{C}^{\text{a}}\text{H}^{\text{a}}\text{NS}.\text{SO}^{\text{a}}\text{KII}$ , which separates on evaporation in yellowish crystals, and may be obtained by recrystallisation in colourless nacreous laminae, decomposing at  $90^{\circ}$ – $100^{\circ}$ . The *silver* and *lead* compounds formed from it by double decomposition likewise decompose very quickly. The potassium salt distilled with strong potash-solution yields ammonia, sulphide and thiosulphate of potassium, and allylamine. With strong sulphuric acid it gives off sulphurous oxide, and an oil boiling at  $140^{\circ}$ , and probably consisting for the most part of allyl sulphide (*Böhler, Ann. Ch. Pharm.* cliv. 59).

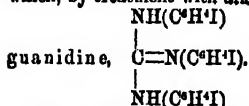
On the use of mustard-oil for preserving milk, see p. 811.

**Phenyl Isosulphocyanate**,  $\text{N}(\text{CS})^{\text{a}}(\text{C}^{\text{a}}\text{H}^{\text{a}})$ . (Losanitsch, *Deut. Chem. Ges. Ber.* iv. 156). An alcoholic solution of *chloraniline*, treated with carbon bisulphide gives

# 1118 SULPHOCYMENIC—SULPHOFUMARIC ACID.

Chlorophenylic sulphocarbamide,  $\text{CS} \begin{Bmatrix} \text{NH}(\text{C}^6\text{H}^4\text{Cl}) \\ \text{NH}(\text{C}^6\text{H}^4\text{Cl}) \end{Bmatrix}$ , and the alcoholic solution of this substance, treated with alcoholic iodine solution, yields chlorophenylic isosulphocyanate or sulphocarbimide,  $\text{N} \begin{Bmatrix} \text{CS} \\ \text{C}^6\text{H}^4\text{Cl} \end{Bmatrix}$ , in colourless needles melting at  $40^\circ$ . This compound reacts with ammonia in the same manner as the other isosulphocyanic ethers, yielding a chlorinated phenyl-carbamide having the composition  $\text{CS} \begin{Bmatrix} \text{NH}(\text{C}^6\text{H}^4\text{Cl}) \\ \text{NH} \end{Bmatrix}$ . Heated with water in sealed tubes to  $130^\circ$ , the chlorophenylic isosulphocyanate is resolved into carbon dioxide, hydrogen sulphide, and chloraniline. With absolute alcohol, on the other hand, it yields a semi-sulphuretted chlorophenylurethane,  $\text{CS}(\text{C}^6\text{H}^4\text{Cl})\text{HN} \begin{Bmatrix} \text{C}^6\text{H}_5 \\ \text{O} \end{Bmatrix}$ .

Iodaniline behaves with carbon bisulphide similarly to chloraniline. In the formation of the corresponding iodated phenylic isosulphocyanate, a residuo is obtained, which, by treatment with alkali and precipitation by acid, gives iodated triphenyl-



A corresponding compound appears also to be formed in the preparation of the chlorophenylic isosulphocyanate.

*Propyl Sulphocyanate*,  $\text{S} \begin{Bmatrix} \text{CN} \\ \text{C}^3\text{H}_7 \end{Bmatrix}$ , formed by treating an alcoholic solution of propyl bromide with potassium sulphocyanate, is a fetid oil boiling at  $163^\circ$  (Carl Schmitt, *Zeitschr. f. Chem.* [2], vi. 576).

**SULPHOCYMENIC ACID.** Syn. with CYMENK-SULPHONIC ACID (p. 420).

**SULPHODIALURIC ACID.** See SULPHOSKUDO-URIC ACID (p. 1125.)

**SULPHODIBROMOBENZENE and SULPHODIBROMONITROBENZENE.** Syn. with DIBROMOBENZENESULPHONIC and DIBROMONITROBENZENESULPHONIC ACIDS (pp. 153, 154).

**SULPHOFORM**,  $\text{C}^2\text{H}^2\text{S}^2$ , appears to be produced by heating sulphur with iodoform in sealed tubes to a temperature not exceeding the melting point of sulphur. On mixing an alcoholic solution of potassium sulphide with chloroform, reaction takes place with explosive violence, and a compound of sulphoform with potassium sulphide is produced, which crystallises from alcohol in long prisms (Pfankuch, *J. pr. Chem.* [2] iv. 38; vi. 97).

**SULPHOFUMARIC ACID**,  $\text{C}^4\text{H}^4\text{SO}^2 = \text{C}^4\text{H}^4\text{SO}^2\text{H}(\text{CO}^2\text{H})^2$ , (Credner, *Zeitschr. f. Chem.* [2], vi. 77). This acid is produced by boiling fumaric acid for a considerable time with a solution of acid potassium sulphite and potassium carbonate. On precipitating the resulting solution with lead acetate, and decomposing the precipitate with hydrogen sulphide, a solution is formed containing an acid potassium salt; to prepare the free acid, this solution must be neutralised with ammonia, and again precipitated with lead acetate.

Sulphofumaric acid forms a syrupy, strongly acid liquid, which, when left for some time over sulphuric acid, deposits indistinct crystals deliquescent immediately on exposure to the air. It is tribasic, and forms basic and acid salts. The *potassium salt*,  $\text{C}^4\text{H}^4\text{K}^3\text{SO}^2 + \text{H}^2\text{O}$ , forms nodular groups of efflorescent crystals. The above-mentioned acid potassium salt likewise forms nodules having the composition  $(\text{C}^4\text{H}^4\text{K}^3\text{SO}^2) \cdot \text{C}^4\text{H}^4\text{SO}^2 + 1\frac{1}{2}\text{H}^2\text{O}$ ; when heated on platinum foil, it swells up like mercuric sulphocyanate. The *acid ammonium salt*,  $\text{C}^4\text{H}^4(\text{NH}^4)^3\text{SO}^2$ , prepared by saturating 1 pt. of the acid with ammonia, and adding 2 pts. of acid, forms crystals. The *silver salt*,  $\text{C}^4\text{H}^4\text{Ag}^3\text{SO}^2$ , obtained by precipitating the neutral potassium salt with silver nitrate, is white, crystalline, and moderately soluble in water. The *barium salt*,  $(\text{C}^4\text{H}^4\text{SO}^2)^2\text{Ba}^2$ , is obtained by precipitation. The *calcium salt*,  $(\text{C}^4\text{H}^4\text{SO}^2)^2\text{Ca}^2 + 6\text{H}^2\text{O}$ , forms colourless efflorescent laminae. The *neutral lead salt*,  $(\text{C}^4\text{H}^4\text{SO}^2)^2\text{Pb}^2 + 4\text{H}^2\text{O}$ , formed by precipitating the acid potassium salt with lead acetate, is soluble in water, free acid, and solution of lead acetate. A basic insoluble lead salt,  $(\text{C}^4\text{H}^4\text{SO}^2)^2\text{Pb}^2 \cdot 2\text{PbO}$ , is obtained by precipitating a solution of the acid potassium salt neutralised with ammonia. The *copper salt* is uncrystallisable.

Sulphofumaric acid heated with strong potash-ley is resolved into sulphurous and fumaric acids. With zinc and hydrochloric acid it gives off hydrogen sulphide. On treating it with hydrochloric acid alone, sulphurous acid is evolved and fumaric acid reproduced.

# SULPHOGALLOLIC—SULPHOPHENYLPROPIONIC ACID. 1119

**SULPHOGALLOLIC ACID**,  $C^6H^4SO^4 = C^6H^3\{(OH)^1\}_{SO^2OH^1}$  (Schiff, *Deut. Chem. Ges. Ber.* v. 642). An acid produced by treating recrystallised pyrogallol with pure disulphuric acid (obtained by adding 1 mol.  $SO^2$  to 1 mol.  $SO^2H^2$ ). A mixture of 25 grams of pyrogallol and 10 a.c. of the acid mixture became hot and solidified in two minutes, and after ten minutes' further warming, the pyrogallol was completely converted into a slightly coloured sulphogallolic acid. This acid is much more soluble than gallic acid, and deliquesces on exposure to the air. Its *potassium salt*,  $C^6H^3(OH)^1SO^2K + 2H^2O$ , crystallises in large rhombic octohedrons. The *silver salt*,  $C^6H^3(OAg)^1SO^2Ag$ , forms crystalline grains.

Sulphogallolic acid when heated, loses water, and is converted into sulphotannic acid,  $C^{12}H^8S^2O^{11} = 2C^6H^4SO^4 - H^2O$  (p. 1125).

**SULPHOMALEIC ACID**,  $C^4H^2SO^2 = C^4H^2(SO^2H)(CO^2H)^2$  (Strecker & Messel, *Zeitschr. f. Chem.* [2], vi. 459). This acid, isomeric with sulphofumaric and sulphosuccinic acid (v. 527), is obtained in indistinct crystals by decomposing its silver salt with hydrogen sulphide. When fused with potash, it yields nothing but fumaric acid. The *neutral potassium salt* has the composition  $C^4H^2K^2SO^2 + H^2O$  (the sulphosuccinate crystallises with  $3H^2O$ ). Its solution gives with lead acetate a heavy white precipitate, which, when decomposed by hydrogen sulphide, yields an *acid potassium salt*,  $C^4H^2KSO^2$ , crystallising from alcohol in small transparent crystals, and precipitated by alcohol from its aqueous solution as a pasty mass, which hardens in the air, and swells up when heated like mercuric sulphocyanate. The solution of this salt, mixed with lead acetate, gives a bulky precipitate of the salt,  $(C^4H^2SO^2)^2Pb^2$ , which becomes crystalline on standing. The *potassium salt* obtained directly in the preparation of the acid by boiling maleic acid with neutral potassium sulphite has the composition  $C^4H^2K^2SO^2$ . The *barium salt*,  $(C^4H^2SO^2)^2Ba^2$ , is slightly soluble in cold, more freely in hot water. A calcium salt with probably 1 at. Ca is obtained by boiling the acid with calcium carbonate; the neutral salt by neutralisation with milk of lime. The *silver salt*,  $C^4H^2Ag^2SO^2$ , prepared from the potassium salt above mentioned by the action of ammonia, forms a heavy precipitate, slightly soluble in cold, more soluble in hot water.

**SULPHOMESITYLENIC ACID**. Syn. with MESITYLENE-SULPHONIC ACID (p. 788).

**SULPHONAPHTHALIC ACID**. Syn. with NAPHTHALENE-SULPHONIC ACID (p. 835).

**SULPHONAPHTHOIC ACID**. See NAPHTHOIC ACID (p. 838).

**SULPHOPALLADATES**. See PALLADIUM (p. 889).

**SULPHOPARA-OXYBENZOIC ACID** (R. Koelle, *Ann. Ch. Pharm.* clxiv. 150-164). This acid is produced by acting with the vapour of sulphuric anhydride on dry para-oxybenzoic acid; a syrupy brown mass is thereby formed, which is to be diluted with water and neutralised with quicklime. The solution of the calcium salt is precipitated with potassium carbonate, and lead acetate is added to the filtrate. The bulky precipitate, which is insoluble in water, is decomposed by hydrogen sulphide, and the solution of the free acid is evaporated on a water-bath. The crude acid thus obtained is purified by dissolving it in absolute alcohol, evaporating the solution, and recrystallising the residue from water. The acid is very soluble in water and alcohol, crystallises in deliquescent, white, silky needles, and gives a blood-red colour with ferric chloride.

On evaporating a solution of the potassium salt, quadratic plates, having the composition  $C^6H^4K^2SO^4 + 2H^2O$ , crystallise out, and from the mother-liquor the salt,  $C^6H^4K^2SO^4 + H^2O$ , is obtained in needles. Both salts contain the same acid, as the latter salt, by addition of caustic potash, may be converted into the quadratic salt, and as both, when fused with caustic potash, yield protocatechuic acid.

The *neutral barium salt*,  $2C^6H^4BaSO^4 + 7H^2O$ , crystallises from water in small plates, and a *basic salt*,  $(C^6H^4SO^4)Ba$ , is obtained as an amorphous powder by adding barium chloride to a solution of the basic potassium salt. The *silver salt*,  $C^6H^4Ag^2SO^4$ , separates from a hot aqueous solution in crystalline flakes. The *copper salt*,  $C^6H^4CuSO^4$ , remains, on evaporating its solution, as a dark-green amorphous powder; the *cadmium salt*,  $C^6H^4CdSO^4 + 3H^2O$ , forms microscopic crystals, and is readily soluble in water.

**SULPHOPHENOLIC ACIDS**. Syn. with PHENOLSULPHONIC ACIDS (p. 917).

**SULPHOPHENYLPROPIONIC ACID**, or **PHENYLSULPHOPROPIONIC ACID**,  $C^9H^7SO^3 = C^9H^6\{(OH)^1\}_{CO^2H^1}$  is formed as an acid potassium salt by the action of neutral potassium sulphite on cinnamic acid:  
 $C^9H^7O^2 + SO^2HK = C^9H^7SO^3K$

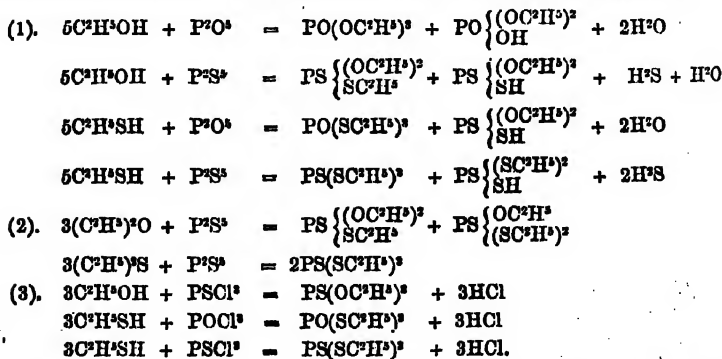
The two bodies unite directly when boiled together for twelve hours in aqueous solution (1 pt. potassium sulphite to 10 water). The *acid potassium salt* crystallises in stellate groups of hard needles, soluble in 25.9 pts. of water at 15°, more easily in hot water, sparingly in alcohol. It crystallises without alteration from boiling dilute hydrochloric or sulphuric acid, melts and decomposes when heated. The *neutral potassium salt*,  $C^3H^3SO^3K^3$  (dried at 120°), crystallises from water in colourless transparent crystals, from alcohol in nodules; it contains water of crystallisation and effloresces in contact with the air. By boiling the acid salt with zinc or zinc oxide, a *zincopotassic salt*,  $(C^3H^3SO^3)^2ZnK^2$ , is produced. The *silver salt* is a white crystalline precipitate. The *lead salt*, obtained by boiling the acid potassium salt with lead hydrate, is a viscid mass while hot, but becomes brittle on cooling.

Phenylsulphopropionic acid, obtained by decomposing the lead salt with hydrogen sulphide, forms colourless easily soluble crystals. It is not altered by boiling with strong hydrochloric or dilute sulphuric acid, but is carbonised by strong sulphuric acid. Strong nitric acid converts it into a nitro-acid. Potassium chromate and sulphuric acid act upon it only in concentrated solution. Strong potash-ley converts it into cinnamic acid (C. Valet, *Ann. Ch. Pharm.* cliv. 62).

**SULPHOPHOSPHORIC ETHERS.** These compounds are phosphoric ethers in which the oxygen is more or less replaced by sulphur. A few of them were obtained by Carius in 1859, by the action of phosphorus pentasulphide on alcohol (iv. 592). More recently (*Ann. Ch. Pharm.* cxix. 289) Carius has obtained nearly the entire series of the ethylsulphophosphoric ethers, and has shown that, both in mode of formation and in chemical reactions, these sulphur-compounds are exactly analogous to the corresponding oxygen-compounds, and that the sulpho-alcohols yield ethers in the same manner as the oxygen-alcohols. Some of the corresponding methyl- and amyl-compounds have been prepared by Kovaletsky (*ibid.* cxix. 303).

The sulphophosphoric ethers exhibit isomerism of such a kind that one of the two bodies has the sulphur, the other the oxygen, outside the radicle; but this difference of structure is not accompanied by any difference of properties; e. g.  $(C^2H^5)^3 \overset{PS}{O}$  is identical in properties with  $(C^2H^5)^3 \overset{PO}{S}$ .

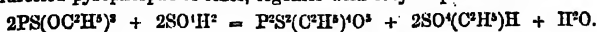
The diethylic and triethylic orthosulphophosphoric ethers are formed: (1), by the action of the hydrates or sulphhydrates; (2), by that of the oxides or sulphides of alcohol-radicles, on the pentoxide or pentasulphide of phosphorus; or (3) by the action of the oxychloride or sulphochloride of phosphorus on alcohol or mercaptan respectively:



1. NEUTRAL OR TRIETHYLIC ORTHOSULPHOPHOSPHORIC ETHERS. These ethers are liquids which do not solidify at  $-18^\circ$ , and have an aromatic odour inclining more and more to alliaceous in proportion to the quantity of sulphur which they contain. Those which contain only oxygen or only sulphur,  $PO(OC^2H^5)^3$ , and  $PS(SC^2H^5)^3$ , volatilise without decomposition, the former at about  $200^\circ$ , as colourless liquids which soon turn red. The three intermediate oxysulpho-ethers,  $PS(OC^2H^5)^2(SC^2H^5)$ ,  $PO(SC^2H^5)^2(OC^2H^5)$ , and  $PS(OC^2H^5)(SC^2H^5)^2$ , are decomposed by heat, giving off ethyl sulphide, with violent ebullition, towards  $160^\circ$ ; the monosulphuretted ether at the same time gives off ethyl oxide and partly distills undecomposed. The mono- and di-sulphuretted ethers distil undecomposed with vapour of water; the tri- and tetra-sulphuretted ethers are decomposed thereby, with evolution of mercaptan and sulphuretted hydrogen. Alkaline and alkaline sulphides, especially in alcoholic solution, convert these neutral

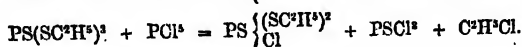
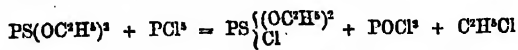


ethers into diethylic acids of the same degree of sulphuration; ethyl tetrasulphophosphate yields at the same time diethylic acids of lower boiling point. The neutral ethers, heated with *alcohol* in sealed tubes, yield the diethylic acid containing 1 at. sulphur less, together with the mono- or di-sulphide of the alcohol-radicle. With strong *sulphuric acid*, the neutral ethers decompose in the following manner, yielding a sulphuretted pyrophosphoric ether, together with ethylsulphuric acid:

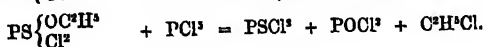
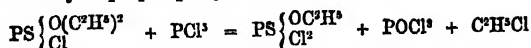


A similar action is exerted by very concentrated solutions of *phosphoric acid* and *calcium chloride*. By the further action of sulphuric acid, sulphur dioxide is evolved and neutral ethers of the metaphosphoric series are produced. Ethylic tetrasulphophosphate, however, does not exhibit the reactions just mentioned.

*Phosphorus pentachloride* forms, with the triethylic orthosulphophosphates, ethyl chloride, phosphoryl chloride—or, in the case of the tetrasulphophosphate, sulphophosphoryl chloride—and a diethylic chloride:



If the pentachloride is in excess, the action goes further, producing a monethylic dichloride, or finally sulphophosphoryl chloride:

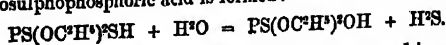


A similar action takes place with phosphorus iodide, or with iodine and phosphorus. The triethylic ethers form well-crystallised compounds with the chlorides and iodides of lead, silver, and especially mercury.

2. **DIETHYLIC ORTHOSULPHOPHOSPHORIC ACIDS.**—*Diethyltetrasulphophosphoric acid*,  $\text{PS}(\text{SC}^2\text{H}^5)^2\text{SH}$ , the end-product of the series, is the only one of these acid ethers which is obtained directly in the pure state; it crystallises in beautiful sulphur-yellow, transparent prisms from its solution in triethylic tetrasulphophosphate, which is the final product of the action of phosphorus pentasulphide on mercaptan. The others have to be separated by hydrogen sulphide from the pure alcoholic solutions of their lead, mercury, or silver salts.

*Diethylmono-* and *Diethyldi-sulphophosphoric acids* are colourless, viscid, very acid liquids, which, when left to evaporate in a vacuum, slowly yield needle-shaped crystals; they smell like butyric acid and deliquesce in contact with the air.

The three acids just described, as well as *diethyltrisulphophosphoric acid*, are decomposed when heated to  $100^\circ$ , with formation of mercaptan. On boiling the aqueous solution of diethyldisulphophosphoric acid, hydrogen sulphide is abundantly evolved, and diethylmonosulphophosphoric acid is formed:



By prolonged boiling the monosulphuretted acid is decomposed in a similar manner.

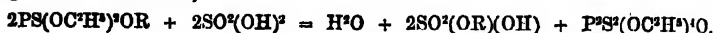
*Diethyltrisulphophosphoric acid* is decomposed by water in like manner, even at ordinary temperatures, and cannot be separated unchanged by evaporation from its alcoholic solution. *Diethyltetrasulphophosphoric acid* decomposes in a similar manner, at the same time that it deliquesces in the air; when it is directly dissolved in water, the recently prepared solution contains small quantities of tetrasulphophosphoric acid.

The four compounds above described belong to the strongest acids. Their salts may be obtained by direct neutralisation of the acid with metallic oxides or carbonates; those which are insoluble, also by precipitation; the diethyltetrasulphophosphates, however, are obtained only by precipitating the ethereal solution of the acid with the ethereal solutions of metallic salts. In the dry state these salts—excepting those of the alkalis and alkaline earths, which are deliquescent—resist perfectly the action of light and air; only the silver and mercury salts of diethyltri- and diethyltetra-sulphophosphoric acid blacken slightly at ordinary temperatures. When heated they decompose with greater facility in proportion as they contain more sulphur; at a red-heat the diethylmonosulphates alone leave the whole of their phosphorus in the form of metaphosphate.

The ammonium, potassium, barium salts, &c., of the four acids are easily soluble

in water; those of diethylmonosulphophosphoric acid with the metals of the magnesium-group, are slightly soluble; all the rest are insoluble and form heavy, curdy precipitates. The last-mentioned salts melt for the most part, without decomposition, and dissolve easily in hot alcohol, ether, or benzene, from which solutions they crystallise very beautifully on cooling. Diethylmonosulphophosphoric acid and its salts in aqueous or alcoholic solution form with ferric salts a brown flocculent precipitate slightly soluble in absolute alcohol; the more highly sulphuretted acids, on the contrary, form deep black crystalline precipitates soluble with ruby-red colour in alcohol.

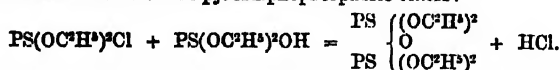
All the salts above described are decomposed by ordinary acids in the cold with great difficulty or not at all; but by strong sulphuric acid, at a gentle heat, they are converted into neutral ethers of the tetrabasic or pyrophosphoric series; thus (R denoting a monatomic metal):



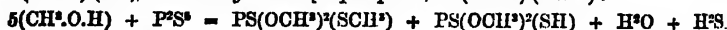
With phosphorus pentachloride they behave like the neutral ethers:



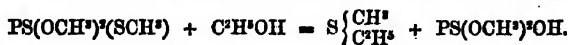
*Ethylsulphophosphoric chlorides.*—The mode of formation of these compounds has been already explained (p. 1121). Only two have actually been obtained, viz.:  $\text{PS}(\text{OC}^2\text{H}^3)^2\text{Cl}$  and  $\text{PS}(\text{OC}^2\text{H}^3)(\text{SC}^2\text{H}^3)\text{Cl}$ . They are heavy, pungent liquids undistillable or not completely distillable without decomposition. They decompose slowly with water, more quickly with alcoholic solutions of the alkalis, forming diethyl chlorides of the diethylated acids; and the bodies of these two classes act on one another in such a manner as to form neutral pyrosulphophosphoric ethers:



3. METHYLIC and AMYLIC ORTHOSULPHOPHOSPHORIC ETHERS (Kovalevsky, *Ann. Ch. Pharm.* cxix. 303).—Methyl alcohol is strongly attacked by phosphorus pentasulphide, and converted, with copious evolution of hydrogen sulphide, into a viscid liquid, which is a solution of *dimethyl-disulphophosphoric acid*,  $\text{PS}(\text{OCH}^3)^2(\text{SH})$ , in *trimethyl disulphophosphate*,  $\text{PS}(\text{OCH}^3)^2(\text{SCH}^3)$ :



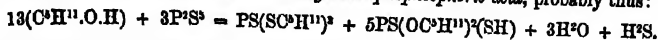
The reaction must at first be moderated by cooling, afterwards promoted by heat, till all the phosphorus sulphide is dissolved. *Trimethyl disulphophosphate*, separated from the product by water, and dried under the air-pump or in a current of air at  $40^\circ$ , is a colourless, oily, fetid liquid, not solidifying at  $-12^\circ$ , slightly heavier than water. It decomposes at  $150^\circ$ , evolving fetid products, but distils almost undecomposed with aqueous vapour; it dissolves easily in dilute alcohol, and in this solution is gradually converted into dimethylphosphoric acid. When heated with alcohol it is resolved into dimethyl-monosulphophosphoric acid and methyl-ethyl sulphide, probably thus:



With *strong sulphuric acid* it forms methylsulphuric acid and an oil separable by water, regarded by Kovalevsky as a mixture of methyl tetrasulphophosphorylphosphate, with an ether of the meta-series. With *phosphorus pentachloride* it yields, together with ethyl chloride and phosphorus oxychloride, a liquid compound—probably dimethyl oxydisulphochloride,  $\text{PS}(\text{OCH}^3)(\text{SCH}^3)\text{Cl}$ —resolved by alkalis into metallic chloride and dimethyl disulphophosphate. With *mercuric iodide* the trimethyl ether forms a compound which crystallises in needles and reacts like the corresponding ethyl-compound.

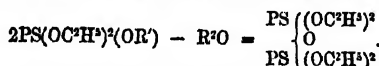
*Dimethyl-disulphophosphoric acid*,  $\text{PS}(\text{OCH}^3)^2(\text{SH})$ , is obtained by digesting the watery liquid separated from the trimethyl ether just described with lead carbonate at  $30^\circ$ – $40^\circ$ , precipitating the filtrate with lead acetate, crystallising the washed precipitate from absolute alcohol, and decomposing the lead salt in alcoholic solution with hydrogen sulphide. On evaporating finally under the air-pump, the dimethylated acid remains as an acid, viscid liquid which decomposes below  $100^\circ$ . The salts which it forms with the alkalis and alkaline earths dissolve easily in water, and are best prepared by treating the lead salt with alkaline sulphides. The dimethyl-disulphophosphates of the heavy metals are curdy precipitates which crystallise from hot ether, alcohol, or benzene. The *lead salt*,  $\text{PS}(\text{OCH}^3)^2\text{SPb}$ , crystallises in shining prisms often an inch long, permanent in the air and melting below  $100^\circ$ . The *mercuric salt*,  $\text{PS}(\text{OCH}^3)^2\text{SHg}$ , is more decomposable and less soluble in alcohol.

Amyl alcohol digested at a gentle heat with phosphorus pentasulphide forms *triethyl tetrasulphophosphate* and *diethyl-disulphophosphoric acid*, probably thus:

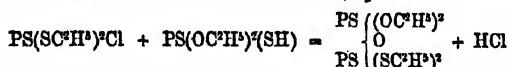


On treating the viscid product with cold water, the acid ether passes into solution, while the triamyl ether separates as a viscid yellow body. The latter is insoluble in water, mixes with absolute alcohol, and decomposes at  $100^\circ$  or when boiled with water. *Diethyl-disulphophosphoric acid*, separated from the aqueous solution in the same manner as the corresponding methyl-compound, is an acid, colourless syrup, already mixed with products of decomposition. Its salts react like those of the dimethyl acid. The lead salt,  $\text{PS}(\text{OC}^2\text{H}^5)^2\text{SPb}$ , melts below  $70^\circ$ , dissolves easily in absolute alcohol, and crystallises in small, four-sided rhombic plates, or in monoclinic prisms.

4. PYROSULPHOPHOSPHORIC ETHERS (Carins, *Ann. Ch. Pharm.* cxix. 298). These ethers are formed: 1. By abstraction of  $(\text{OC}^2\text{H}^5)^2$  from 2 mols. of a neutral ortho-sulphophosphoric ether, by the action of strong sulphuric acid, &c. (p. 1025). 2. By abstraction of the elements of a metallic oxide,  $\text{R}^2\text{O}$  or  $\text{R}'^2\text{O}$ , from 2 mols. of a salt of a diethyl acid of the ortho-series, by the action of hydrogen sulphate on phosphorus oxychloride (a very large excess of salt being used in the latter case):



3. By the action of the diethyl-chlorides of the ortho-series on the diethyl acids of the same series, or on their salts, or neutral ethers, e.g.:



*Tetreehlyic Disulphopyrophosphate*,  $(\text{PS})^2(\text{OC}^2\text{H}^5)^4\text{O}$ , is a colourless, nearly scentless oil, moderately soluble in water without decomposition; it begins to boil, with simultaneous decomposition, somewhat below  $160^\circ$ . On distilling it with vapour of water, the greater part passes over undecomposed, while the remainder takes up the elements of water, and is converted into *diethyl-orthosulphophosphoric acid*. Treated with a quantity of alcoholic potash not sufficient to decompose it completely, it is converted into *potassium triethyl-disulphopyrophosphate*, from which the free acid cannot be separated without alteration, since at the moment of separation it takes up the elements of water.

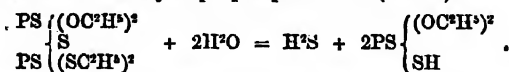
*Trisulphopyrophosphoric Bromotriethylin*,  $\text{P}^2\text{S}^3(\text{OC}^2\text{H}^5)^3\text{Br} = \begin{matrix} \text{C}^2\text{H}^5\text{O} \\ \text{C}^2\text{H}^5\text{O} \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{PS} - \text{S} - \text{PS} \begin{matrix} \diagdown \\ \diagup \end{matrix} \begin{matrix} \text{OC}^2\text{H}^5 \\ \text{Br} \end{matrix}$ .—This compound is formed when pyrophosphoric sulphobromide (p. 063) is slowly poured into alcohol distilled from sodium. The resulting liquid when poured into water yields a yellow oil consisting of the two ethers,  $\text{P}^2\text{S}^3(\text{OC}^2\text{H}^5)^3\text{Br}^2$  and  $\text{P}^2\text{S}^3(\text{OC}^2\text{H}^5)^3\text{Br}$ . But on redissolving it in alcohol, leaving the solution to stand for some time, and again pouring it into water, only the triethylated body is obtained, the substitution of ethoxyl for bromine taking place with difficulty in presence of much hydrogen bromide.

The bromotriethylin is a yellow, transparent liquid having an ethereal odour, recalling however that of the sulphobromide. Its specific gravity is 1.3567 at  $19^\circ$ . It cannot be distilled without decomposition, and it fumes slightly in the air after exposure to it for some time. It is slowly decomposed by water and aqueous alkalis, with separation of sulphur. Alcoholic solutions decompose it more quickly, producing mercaptan-like bodies, phosphoric acid, and bromide of the metal (Michaelis, *Ann. Ch. Pharm.* clxiv. 9).

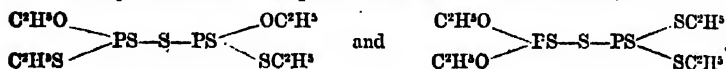
*Tetreehlyic Trisulphopyrophosphate*,  $\text{PS}^3(\text{OC}^2\text{H}^5)^4 = \begin{matrix} \text{C}^2\text{H}^5\text{O} \\ \text{C}^2\text{H}^5\text{O} \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{PS} - \text{S} - \text{PS} \begin{matrix} \diagdown \\ \diagup \end{matrix} \begin{matrix} \text{OC}^2\text{H}^5 \\ \text{OC}^2\text{H}^5 \end{matrix}$ , is formed by the further action of alcohol on the triethylated bromide just described. The latter is dissolved in three times its volume of alcohol, and the solution, after being left for some hours, at  $40^\circ$ , and then cooled, is precipitated by water. It is a yellow, faintly aromatic liquid, smelling somewhat like turpentine. Sp. gr. 1.1892 at  $170^\circ$ . It can be distilled with steam with only partial decomposition. Heated to  $60^\circ$  with alcoholic ammonia in a sealed tube, it is decomposed, yielding a white amorphous substance, which is probably the amide,  $\text{PS}^3(\text{NH}^2)^4$  (Michaelis).

*Ethylic Tetrasulphopyrophosphate* has not yet been obtained pure; it appears to be a solid, easily fusible body (Carius).

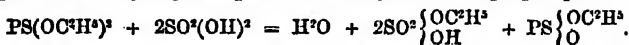
*Tetreethyl Pentasulphopyrophosphate*,  $P^2S_5(OC^2H^5)^4(SC^2H^5)^2$ , is formed by the action of strong sulphuric acid on triethylic disulphorthophosphate (p. 1120) (Carius). It is also deposited during the drying of the trisulphopyrophosphoric ether just described, in small white crystals, and may be separated from the liquid by filtration through asbestos. It is obtained in much larger quantity by treating trisulphopyrophosphoric sulphobromide at  $40^\circ$ , with aqueous instead of absolute alcohol, and most abundantly of all by the action of alcohol on the impure metaphosphoric sulphobromide obtained in the preparation of the pyrobromide (p. 963). In this case there appears to be no action at first, but after some time the mixture becomes hot, the greater part of the metabromide disappears, and as the liquid cools, the tetreethylic pentasulphopyrophosphate separates out in large crystals (Michaelis). It melts at  $71.2^\circ$ , and is especially distinguished by the facility with which it may be converted into a salt of diethylsulphophosphoric acid (Carius):



Theoretically, it should be susceptible of two isomeric modifications, viz.:



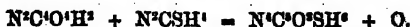
5. **ETHYLIC MONOSULPHOMETAPHOSPHATE**,  $PS \left\{ \begin{array}{l} OC^2H^5 \\ O \end{array} \right.$ , is formed by the prolonged action of hydrogen sulphate on tetreethylic monosulphophosphate:



**SULPHOPYROTARTARIC ACID**,  $C^2H^2SO^4$  (T. Wieland, *Ann. Ch. Pharm.* clvii. 34). This acid is formed by direct combination of the three isomeric pyrocitric acids,  $C^2H^2O^4$ , with alkaline sulphites. When neutral potassium sulphite is boiled for several hours in moderately concentrated solution with itaconic acid, potassium sulphopyrotartrate is formed, and may be obtained in the form of a syrup by evaporation, or as a gummy mass by precipitation with alcohol. Its solution gives pasty precipitates with barium or lead acetate, but is not precipitated by iron, copper, mercury, or zinc salts. With calcium chloride it gives a crystalline calcium salt,  $(C^2H^2SO^4)^2Ca + 7H^2O$ , which gives off 5 mols. water at  $110^\circ$ , another at  $160^\circ$ , becomes anhydrous at  $180^\circ$ , and decomposes between  $190^\circ$  and  $200^\circ$ . It dissolves easily in hot, sparingly in cold water. By treating it with sulphuric acid and dilute alcohol, and evaporating the filtrate, sulphopyrotartaric acid is obtained in indistinct crystals. By partially neutralising the acid with carbonate of potassium or ammonium, acid salts are obtained in nodular groups of crystals, easily soluble in water, less soluble in dilute alcohol, quite insoluble in strong alcohol.

Citraconic and mesaconic acids treated with potassium sulphite yield sulpho-acids, which appear to be identical with that obtained from itaconic acid.

**SULPHOPSEUDO-URIC ACID**,  $C^2H^2N^2SO^4$  (Nencki, *Deut. Chem. Ges. Ber.* iv. 722; v. 451). This acid is obtained by heating a mixture of 2-3 grms. sulphocarbamide and the equivalent quantity of alloxan, with concentrated alcoholic solution of sulphurous anhydride in sealed tubes to  $100^\circ$  for about five hours. The product is purified by repeated treatment with concentrated ammonia to remove uramil; dissolution in caustic soda, rise of temperature being carefully avoided; filtration; precipitation with solution of ammonium chloride, to remove sulphur; and recrystallisation from very concentrated hydrochloric, or better hydrobromic acid, from which it separates on cooling in concentric groups of slender needles. It is probably formed according to the equation:



Sulphopseudo-uric acid is insoluble in water and ammonia, difficultly soluble in hydrochloric, but more readily in hydrobromic and sulphuric acids, being reprecipitated on the addition of water. All attempts to remove the sulphur from it have been unsuccessful. It is readily soluble in the fixed alkalis, even in the cold; on warming, the solution becomes yellow, and then contains the alkaline salt of a compound, precipitable from the very dilute solution by hydrochloric acid in the form of silky, glistening, microscopic plates, which on analysis gave numbers agreeing both with the formula of hydrated sulphoalloxantin,  $C^2N^2SO^2H^2 + 2nq$ , and of sulphodialuric

acid,  $C^6H^4SO^2H^1 + 1\frac{1}{2} aq.$  The instability of this substance renders a determination of the water of crystallisation difficult.

When sulphopseudo-uric acid is heated with twice its weight of strong sulphuric acid to  $150^\circ$ – $160^\circ$ , a small quantity of sulphurous oxide is evolved, and urosulphinic acid,  $C^6H^4N^1SO^2$ , is formed—a weak monobasic acid, derived from sulphopseudo-uric acid by abstraction of  $H^2O$ , and intermediate in chemical character between uric acid and xanthine. If the heating with sulphuric acid be continued, and the temperature raised to  $200^\circ$ , much sulphurous oxide is evolved, the yield of urosulphuric acid is but small, and the solution when evaporated yields a new compound also containing sulphur.

**SULPHOSALICYLIC ACID,  $C^7H^5SO^2$ .** When pure salicylic acid is dissolved in ordinary sulphuric acid at a very little heat, and the product is neutralised with calcium carbonate, filtered from gypsum, precipitated by potassium carbonate, decolorised by animal charcoal, and allowed to crystallise, prismatic crystals are obtained, which have the composition  $C^7H^5O^4SK^2 + 2H^2O$ , do not give off their water of crystallisation below  $190^\circ$ , and begin to decompose at  $200^\circ$ . The mother-liquors of this salt yield another salt which crystallises in quadrate tables very different from the prisms of the former salt; it is much more soluble, and contains  $C^7H^5O^4SK^2 + 1\frac{1}{2}H^2O$ , the water of crystallisation being given off at  $180^\circ$ , and decomposition commencing at  $190^\circ$ . Neither salt is altered in character by further recrystallisation. Fused potassium hydrate does not act on these compounds so readily as on compounds which contain fewer substituted groups (Ira Ramsen, *Zeitschr. f. Chem.* vii. 296).

**SULPHOSUCCINIC ACID,  $C^4H^4SO^2$ .** According to Messel (*Ann. Ch. Pharm.* clvii. 15), this acid, prepared by Fehling's method (v. 527), is identical with sulphomaleic and sulphofumaric acid (p. 1118). Its neutral potassium salt,  $C^4H^3K^1SO^2$ , however, crystallises with  $3H^2O$ , whereas the corresponding salts of the other two acids contain only 1 mol. water. Sulphosuccinic acid is converted by fusion with potash into fumaric acid, and by boiling with potash, in the first instance into malic acid (Strecker u. Messel, *Zeitschr. f. Chem.* [2], vi. 671).

**SULPHOTANNIC ACID,  $C^{12}H^8SO^{11}$ ,** is formed by dehydration of sulphogallollic acid,  $C^{12}H^8SO^6$  (p. 1119), and may be obtained by gradually heating the crude product of the action of pyrosulphuric acid on pyrogallol with phosphorous chloride to  $100^\circ$  in a flask with reversed condenser. Hydrochloric acid is then given off, and the liquid, after 3 or 4 hours, solidifies to a violet gelatin, which dries up to white floccs over sulphuric acid. Sulphotannic acid closely resembles tannic acid. By boiling with hydrochloric acid it is converted into sulphogallollic acid. Its acetyl-derivative does not exhibit the reactions of tannic acid (Schiff, *Deut. Chem. Ges. Ber.* v. 861).

**SULPHOTEREPHTHALIC ACID,  $C^8H^4SO^2 = C^8H^4\begin{matrix} SO^2H \\ CO^2H \end{matrix}$**  is prepared by heating terephthalic acid to  $200^\circ$  for six hours with strong sulphuric acid. The barium salt, obtained by pouring the product into water and neutralising the filtrate with barium carbonate, has the composition,  $[C^8H^4(CO^2H)SO^2]^2Ba$ . When the potassium salt prepared from it is fused with sodium formate, much sulphurous oxide is given off and terephthalic acid is reproduced (Ascher, *Ann. Ch. Pharm.* clxi. 2).

**SULPHOTOLUENE,  $C^7H^5SO^2$ .** Syn. with TOLUENE-SULPHONIC ACID (q. v.)

**SULPHOTOLUIDE,  $C^6H^4SO^2 = C^6H^4\begin{matrix} ClH^1 \\ SO^2 \\ CH^3 \end{matrix}$**  This compound, which

Deville obtained by the action of fuming sulphuric acid on toluene (*Ann. Ch. Pharm.* xlv. 306), has been further examined by Otto a. Gruber (*ibid.* cliv. 193). It crystallises from hot alcohol in small tabular prismatic forms, from benzene in vitreous monoclinic prisms; melts at  $155^\circ$ – $156^\circ$ ; is insoluble in water, slightly soluble in cold alcohol and ether, more soluble in boiling alcohol, benzene, carbon sulphide; and chloroform. It volatilises in small quantities without decomposition; is converted by heating with strong sulphuric acid into toluene-sulphonic acid; dissolves without decomposition in fuming nitric acid; and when heated with a mixture of sulphuric and nitric acids, yields crystallisable nitro-products. It is not altered by strong alcoholic potash even at  $160^\circ$ . Exposed to the action of chlorine in sunshine it deliquesces to an oily mass, probably containing sulphuryl chloride. With chlorine, in diffused daylight, at its melting point, it forms hydrochloric acid and chlorinated products not yet examined. With phosphorus pentachloride it reacts in a similar manner.

**SULPHO-UREAS.** See SULPHOCARBAMIDES (p. 1115).

**SULPHOVALERALDEHYDE**,  $C^3H^4S$ . See VALERALDEHYDE.

**SULPHOXYANTHRAQUINONIC ACID**,  $C^{14}H^6(O^2)(OH)(SO^2H)$ . See 1st Suppl. p. 84.

**SULPHOXYALO-ACIDS.** See SULPHAZOTISED ACIDS (p. 1111).

**SULPHOXYBENZOIC ACID**,  $C^7H^5O^2SO^2$ . This acid, prepared by the action of sulphuric acid on pure oxybenzoic acid, yields, when fused with potash, protocatechuic acid (p. 431) and an isomeric acid less soluble than protocatechuic acid, and forming large, compact, apparently quadratic crystals containing water of crystallisation which is given off at  $140^\circ$ . The acid melts at  $189^\circ$  and gives no coloured reaction with ferric chloride (Ira Remsen, *Zeitschr. f. Chem.* [2], vii. 294).

**SULPHUR.** *Occurrence.*—This element has been detected spectroscopically in the sun's atmosphere by C. A. Young (*Sill. Am. J.* [3], iv. 356).

The presence of sulphur in Coal-gas may be exhibited by placing a platinum dish containing water over a Bunsen burner, the part of the surface on which the flame impinges becoming coated with a greasy liquid in which sulphuric acid may be detected (Ulex, *Jahresb. f. Chem.* 1871, 207).

On sulphur in Pig-iron, see IRON (pp. 604, 695).

*Extraction.*—On the extraction of sulphur from sulphuretted ores by roasting, see Tessié du Mothay (*Dingl. pol. J.* cxci. 221); Hasenclover u. Illebig (*ibid.* 284; *Jahresb. f. Chem.* 1871, 980).

On the recovery of sulphur from Soda-waste, see L. Mond (*Dingl. pol. J.* ccii. 266; *Jahresb.* 1871, 1016); Stahlhelm (*Dingl. pol. J.* cxi. 375; *Jahresb.* 1872, 977).

*Physical Properties.*—On the Spectrum of Sulphur vapour, see Salet (*Compt. rend.* lxxiii. 559; *Chem. Soc. J.* [2], ix. 1145; x. 382; *Jahresb.* 1871, 165; 1872, 141); Ditto (*Compt. rend.* lxxiii. 622; *Chem. Soc. J.* [2], ix. 1146; *Jahresb.* 1871, 170); Gernez (*Compt. rend.* lxiv. 803; *Chem. Soc. J.* [2], x. 382; *Jahresb.* 1872, 139).

On the Heat evolved in the combination of Sulphur with Oxygen, see HEAT (pp. 608-613), with Hydrogen (p. 615).

On the Specific Heat of Sulphur dissolved in Carbon Bisulphide (p. 601).

*Modifications.*—The properties of amorphous sulphur (v. 531) have been examined by R. Weber (*Pogg. Ann.* cxli. 432). Sulphur, separated from a solution of 1 pt. sodium thiosulphate in  $\frac{1}{2}$  to 3 pts. water at about  $10^\circ$ , by stirring with hydrochloric acid, is, a short time after its preparation, almost entirely liquid. The liquid sulphur separated by pressure from a small solidified portion has the colour and consistence of yolk of egg, a specular surface, and a sp. gr. of 1.920, 1.927, 1.926. It solidifies after 24 hours, or sooner, and with evolution of heat, if heated to  $100^\circ$ . The liquid sulphur dissolves almost entirely in carbon sulphide, but the sulphur left on evaporating the solvent contains a portion which no longer dissolves in the carbon sulphide. Stirring the liquid sulphur during solidification renders it partly insoluble in carbon sulphide, the undissolved portion separating as an oily liquid which soon solidifies to a compact or pulverulent mass, accordingly as it has been left at rest or stirred during solidification. If the sulphur, after being brought into a turpentine-like consistence by stirring, be kneaded between the fingers, it becomes very hot, brittle, and crystalline, and then contains a small proportion insoluble in carbon sulphide. The same change is produced in the soft sulphur by diffusing it in a liquid. The sulphur deposited in thin crusts after separation of the greater part of the oily sulphur from the acid solution of the sodium salt, sometimes contains as much as 36 p.c. of insoluble sulphur. Weber regards these results as unfavourable to the supposition that the insoluble sulphur is an immediate product of decomposition of the thiosulphuric acid. Liquid sulphur, separated in the manner above described, almost always contains a small quantity of hydrogen persulphide, which has some influence on the maintenance of the liquid state, like that exerted, according to Diezenbacher (*Jahresb.* 1862, 58; 1865, 127), by small quantities of iodine, bromine, carbon, organic matters, &c.

Sulphur melted with addition of  $\frac{1}{4}$  p.c. sulphur chloride, forms, when poured into water, a soft mass which hardens after a few days like ordinary cooled sulphur, and when heated in a water-bath, first becomes almost completely fluid and then solidifies to a crystalline mass with evolution of heat. In this respect it behaves like ordinary soft sulphur, requiring only a somewhat longer time for the transformation, and remaining longer fluid. When immersed in carbon sulphide it is converted into a doughy, ropy mass which partly dissolves, leaving a residue of the consistence of insoluble liquid sulphur, quickly solidifying and converted into a powder by stirring. Sulphur fused with  $\frac{1}{4}$  p.c. sulphur chloride and slowly cooled is solid, crystalline, and

otherwise like that above described. Weber's observations do not confirm the statement that crystalline sulphur becomes amorphous in contact with acids, or the view advanced by Berthelot (v. 530), that the sulphur which forms the 'electro-negative element of a compound separates therefrom in the soluble state, whereas that which forms the electro-positive element separates in the insoluble state. Sulphur separated from potassium polysulphide by very dilute nitric acid was found by Weber to contain 86 p.c. soluble sulphur; that which was separated in like manner from hydrogen sulphide contained 74 p.c. insoluble sulphur.

*Conversion of Octohedral into Insoluble Sulphur by the action of Sunlight.*—When sunlight concentrated by a lens is passed through a solution of sulphur in carbon sulphide contained in a sealed vessel, there is formed at the point where the rays enter the solution, a yellow spot of insoluble sulphur which quickly increases, and at the same time the intensity of the emergent light continually diminishes. Along the whole path of the rays, and especially at the focus, the solution becomes turbid, in consequence of the separation of extremely fine particles of insoluble sulphur. In the spectrum of the emergent light, all the rays between G and H are wanting, as well as the whole of the ultraviolet rays, whereas the part of the spectrum from A to G remains unaltered. It appears, therefore, that the chemical rays are absorbed and expended in molecular work (Lallemand, *Compt. rend.* lxx. 182).

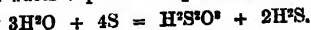
*Blue Sulphur.*—It is well known that when sulphur is brought in contact with sulphuric anhydride in a certain proportion (1 : 10) a blue liquid is formed. According to W. Stein (*J. pr. Chem.* [2], vi. 178), the colour is due to the circumstance that the sulphur is diffused through the anhydride in a state of very fine division, and may remain suspended in the liquid for weeks like gold-purple. That finely divided sulphur really has a blue colour may be shown by adding a small quantity of ferric chloride to a recently prepared solution of sulphydric acid, the liquid then appearing blue. It is only in transmitted light that the sulphur exhibits this blue colour, and the same is the case with the blue compound of sulphuric anhydride.

*Solubility.*—Sulphur (in the form of flowers) does not dissolve in a solution of sodium carbonate (containing 5.6 p.c.  $\text{Na}^2\text{CO}^3$ ), at  $25^\circ$ , but after ten hours' digestion at  $100^\circ$ , the liquid contains 0.0676 p.c. sulphur (Pohl, *Dingl. pol. J.* cxvii. 508).

*Linseed oil mixed with sulphur dissolves the following quantities:*

Temperature	$25^\circ$	$60^\circ$	$95^\circ$	$130^\circ$	$160^\circ$
Sulphur p.c. dissolved	0.630	1.853	2.587	4.935	9.120

*Reactions.* 1. With Vapour of Water.—According to J. Myers (*Compt. rend.* lxxiv. 195), the action of steam on sulphur at high temperatures produces, not pentathionic acid, as stated by Mulder (*Jahresb.* 1858, 84), but thiosulphuric acid. When steam is passed over boiling sulphur, a slightly acid distillate is obtained, holding in suspension sulphur, which may be removed by agitation with white lead. The filtered solution is resolved at  $30^\circ$  into sulphuric acid and free sulphur, gives a black precipitate with mercurous nitrate, a precipitate of copper sulphide with cupric sulphate, and decolorises iodine-solutions. As this property is not exhibited by tri-, tetra-, or pentathionic acid, but only by sulphurous and thiosulphuric acids, and since the acid in the distillate is resolved by heat into sulphurous acid and sulphur, its identity with thiosulphuric acid is established. That this acid can exist in very dilute aqueous solution is shown by the experiments of H. Rose and Flückiger (v. 629). The reaction between sulphur and water-vapour takes place according to the equation:



Myers also finds that gases, dried by the ordinary means (calcium chloride, strong sulphuric acid, phosphoric anhydride), when passed over boiling sulphur, always give rise to the formation of hydrogen sulphide, and must therefore still contain moisture. He thence infers that the synthesis of hydrogen sulphide from hydrogen and sulphur, observed by many chemists, is really due to the small quantity of moisture which remains in gases, even after they have been subjected to the action of the most powerful desiccating agents (*Deut. Chem. Ges. Ber.* v. 259).

2. With Mercury-vapour.—A. B. v. Schrotter (*Wien Akad. Ber.* [2 Abth.], lxi. 79; *Jahresb.* 1872, 268) finds that when a few lumps of sulphur are introduced into a barometric vacuum (which is filled with mercury vapour) the tube near the surface of the mercury becomes coated with a ring of mercuric sulphide. Also when mercury and sulphur are placed together under a bell-jar the sulphur becomes blackened, showing that the jar is filled with mercury-vapour, which is absorbed by the sulphur. When iodine, mercury and sulphur are placed under a bell-jar in separate dishes, the mercury soon becomes covered with a coating of iodide, while the sulphur remains unaltered for weeks.

The use of flowers of sulphur has been recommended for removing mercury-vapour from the atmosphere of workshops in which glass mirrors are made. According to Merget, however, sulphur is not very efficacious for this purpose, and a better result is obtained by the use of bleaching powder, a small quantity of which scattered about a room infected with mercury-vapours removes the mercury in the form of calomel (*Dingl. pol. J.* cciv. 51; *Chem. Soc. J.* [2], x. 923).

3. On the action of melted sulphur on an alloy of gold and silver, see p. 576.

4. On Carbon tetrachloride. The reaction takes place readily at 130°, according to the equation:



(Gustavson, *Zeitschr. f. Chem.* [2], vii. 418).

*Estimation of Sulphur.*—Important observations on the precipitation of sulphur as barium sulphate, in presence of various salts, have been made by R. Fresenius (*Zeitschr. anal. Chem.* ix. 52). Barium sulphate is not, as hitherto supposed, soluble in 4,300 pts. of water, but requires for solution more than 400,000 parts. The solubility is not perceptibly increased by the presence of sodium chloride, potassium chlorate, or barium nitrate, but hydrochloric acid produces a sensible increase. Sodium chloride, mixed with the solution of a sulphate, does not give rise to any impurity in the precipitation of the sulphuric acid as barium sulphate, neither is the result in this case affected by the presence of more or less hydrochloric acid. Potassium chlorate gives rise to great contamination, but the precipitate, after ignition and cooling, may be completely purified by digestion with hydrochloric acid; as, however, barium sulphate is somewhat soluble in hydrochloric acid, the filtrates must be evaporated down to determine the quantity of barium salt dissolved in them. In presence of potassium nitrate, or sodium nitrate, the precipitated barium sulphate is very impure, whether the quantity of hydrochloric acid present, and of barium chloride added, be large or small. The only way of purifying the precipitate thus contaminated is to disintegrate it by fusion with sodium carbonate, and estimate the sulphuric acid in the aqueous solution of the fused mass. If it be desired to avoid this circuitous process, the original substance must be completely freed from nitric acid by repeated evaporation with pure hydrochloric acid, and the hydrochloric acid almost wholly driven off before proceeding to the precipitation with barium chloride. Barium nitrate likewise gives rise to contamination, but the precipitate after ignition may be purified by digestion with hydrochloric acid; regard must, however, be had to the solubility of barium chloride in hydrochloric acid. The purification of the precipitated barium sulphate by Stolla's method (digestion with solution of cupric acetate containing free acetic acid, *Jahresb.* 1863, 669), is, according to Fresenius, not to be depended on.

*Volumetric method.*—On account of the difficulty of obtaining a pure precipitate of barium sulphate in presence of other salts, J. Denham Smith and E. F. Teschemacher (*Chem. News* xxiv. 61, 66, 171; *Chem. Soc. J.* [2], ix. 1085) have proposed a volumetric method for the estimation of sulphur—in pyrites, for example. For this purpose they prepare a standard solution of barium chloride, and determine its strength by allowing it to flow into boiling dilute sulphuric acid, and weighing the precipitate. When precipitated in this way the barium sulphate contains scarcely any chlorine, whereas, if the precipitation be performed in the contrary way, it always contains an appreciable quantity of chlorine. The strength of the barium solution having been determined, the liquid to be tested is heated, and precipitated with it, till a filtered sample is no longer clouded by the barium solution, the sample of liquid being poured back after each experiment. The quantity of the barium solution used gives the quantity of sulphuric acid in the liquid under examination.

Glendinning a. Edger (*Chem. News* xxiv. 140) are of opinion that in applying this method to the estimation of sulphur in pyrites, errors may arise from the fact that the precipitated barium sulphate carries down with it a certain quantity of iron sulphate, and they adduce experiments tending to show that when this salt is washed out of the precipitate by water and hydrochloric acid, the sulphur in the washings reprecipitated by barium chloride, and the small precipitate of barium sulphate thus obtained added to the original precipitate, concordant results may be obtained.

The following were the results of the analyses of four samples of pyrites:—25 grains were carefully oxidised and precipitated by barium chloride in the usual way. The precipitated liquors were left in a warm place for eight hours, then filtered, and the barium sulphate was washed with boiling water and hydrochloric acid. The whole of the washings, after addition of a little barium chloride, were evaporated to dryness, and the quantities of barium sulphate obtained, amounting generally to 0.5 grain, added to the original precipitates, three of which, after ignition and weighing, were treated with about 600 grs. of strong hydrochloric acid, and allowed to



stand for twelve hours. The small quantities of sulphate dissolved by the acid were recovered, and added to their respective precipitates.

No.	Before treatment with HCl		After treatment with HCl	
	Grs. BaSO <sup>4</sup>	Grs. S	Grs. BaSO <sup>4</sup>	Grs. S
1	83.12	11.415	83.08	11.411
2	83.18	11.423	83.12	11.415
3	83.30	11.440	83.23	11.430
4	83.23	11.430	—	—

A reply to these observations is given by Smith a. Teschemacher (*Chem. News*, xxiv. 171), and a rejoinder by Glendinning a. Edger (*ibid.* 220).

**Estimation of Sulphur in Coal Gas.**—A. Vernon Harcourt (*ibid.* xxii. 307) determines sulphur in coal gas by causing a Bunsen flame  $\frac{1}{2}$  of an inch long, and consuming  $\frac{1}{2}$  cubic foot in an hour, to burn within a cylinder connected with an aspirator. The gaseous products of combustion thus drawn off pass through a series of vessels containing an ammoniacal solution of cupric oxide, which takes up the sulphurous and sulphuric acids, and oxidises the former. After about two cubic feet of gas have been consumed, the liquid is decanted into a beaker, the vessel rinsed with water, the greater part of the ammonia expelled by heat, and the sulphur precipitated by barium chloride.

(On the estimation of sulphur in Coal and Coke, see COAL (p. 347); in Coal and Organic Bodies, see MIXTER (*Sill. Am. J.* [3], iv. 90; *Chem. Soc. J.* [2], x. 1114; *Jahresb.* 1872, 918). On its estimation in Pig-iron, see IRON (p. 692).

**SULPHUR, CHLORIDES AND OXYCHLORIDES OF.** The existence of three distinct compounds of sulphur with chlorine—viz.: *Sulphur sulphodichloride*, S<sup>2</sup>Cl<sup>2</sup>, *Sulphur dichloride*, SCI<sup>2</sup>, and *Sulphur tetrachloride*, SCI<sup>4</sup>—appears to be now placed beyond doubt by the recent researches of Huebner a. Guerout, Dalczell a. Thorpe, and Michaelis.

Thus Huebner a. Guerout (*Zeitschr. f. Chem.* 1870 [2], vi. 455) find that, if pure sulphur sulphodichloride, S<sup>2</sup>Cl<sup>2</sup> (b. p. 136.5°–137° uncor.), cooled by a good refrigerating mixture of ice and salt, is saturated with chlorine, and a current of carbonic anhydride then passed through the liquid for several hours, a product is obtained having the composition required by the formula SCI<sup>2</sup>, viz.: 30.5 p.c. of sulphur and 69.3 p.c. of chlorine, the theoretical amounts being 31.07 and 68.93. Dalczell a. Thorpe (*Phil. Mag.* 1871, 309; *Jour. Chem. Soc.* [2], ix. 1163) have repeated this experiment with precisely the same result, finding 69.25 and 69.06 p.c. of chlorine in the products they obtained.

Michaelis (*Ann. Ch. Pharm.* clxx. 6) has since shown that when sulphur sulphodichloride is saturated with chlorine at about –20°, the amount of chlorine absorbed corresponds with that required to form sulphur tetrachloride, and the product actually has the composition SCI<sup>2</sup>. Thus 67.5 grams S<sup>2</sup>Cl<sup>2</sup> absorbed 106 grams of chlorine, the amount required by theory being 106.5 grams; and taking the mean of two analyses, the product contained 81.59 p.c. of chlorine and 18.41 p.c. of sulphur, the theoretical numbers being 81.61 and 18.39.

Michaelis has studied the dissociation of sulphur dichloride and sulphur tetrachloride. The results which he obtained, together with the earlier observations of Carius, which are denoted by a \*, are included in the following tables:

	Cl	S
SCI <sup>2</sup>	81.61	18.39
At –22°	81.59	18.41
–15	74.21	25.79
–10	72.39	27.61
* –7	71.67	28.33
* –2	70.39	29.61
* 0.7	70.00	30.00
* 0.2	69.18	30.82

## SULPHUR: CHLORIDES

*Dissociation of Sulphur Dichloride.*

	Cl <sup>2</sup>	S
SCl <sup>2</sup>	68.13	31.13
* 20	67.80	32.20
30	66.80	33.20
50	64.85	35.15
65	63.44	36.56
85	61.36	38.64
90	58.85	43.15
100	55.70	44.30
110	54.54	45.45
120	53.41	46.59
130	52.43	47.57
S <sup>2</sup> Cl <sup>2</sup>	52.59	47.41

From these numbers the percentage of SCl<sup>2</sup> and SCl<sup>2</sup> existing in the mixtures at the various temperatures is calculated by the aid of the formulae:

$$0.8161x + (100 - x)0.6887 = A,$$

$$0.6887x + (100 - x)0.5259 = A',$$

where  $x$  is the percentage of SCl<sup>2</sup> or SCl<sup>2</sup>, and  $A$  and  $A'$  the percentage of chlorine found at the various temperatures, thus:

*Dissociation of Sulphur Tetrachloride.*

Temp.	Diff.	SCl <sup>2</sup>	SCl <sup>2</sup>	Diff.	Increase for 1°
-22°		100.00	0.00		
-15	7°	41.95	58.05	58.05	8.3
-10	5	27.62	72.38	13.32	2.6
* -7	3	21.97	78.03	5.66	1.9
* -2	5	11.93	88.07	10.04	2.0
* 0.7	2.7	8.87	91.13	3.06	1.1
* 6.2	6.5	2.43	97.57	6.44	1.1

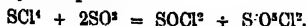
*Dissociation of Sulphur Dichloride.*

Temp.	SCl <sup>2</sup>	S <sup>2</sup> Cl <sup>2</sup>	Diff. for 10°	Calculated
*20°	93.45	6.55		6.00
30	87.22	12.78	6.23	12.19
50	76.41	24.59	6.41	24.57
65	66.78	33.22	5.79	33.85
85	54.06	45.94	6.36	46.13
90	26.48	73.52		73.52
100	19.45	80.55	7.03	80.53
110	12.85	87.65	7.10	87.54
120	5.44	94.56	6.91	94.55
130	0.00	100.00	5.44	—

The loss of chlorine by sulphur tetrachloride thus takes place with great rapidity, but the dichloride is much more stable. It will be noticed, in the case of sulphur dichloride, that the increase of decomposition is constant for equal elevations of temperature between 20° and 85°, but that it suddenly rises very quickly between 85° and 90°, from which temperature to 130° it takes place at the previous rate. The cause of this phenomenon has not been ascertained. The course of the dissociation of sulphur dichloride between 20° and 85° may be represented by the linear equation  $y = 0.619x + 6.693$ , and between 90° and 130° by  $y = .701x + 10.43$ . If in the first equation  $y = 0$ ,  $x$  will be 10.8—that is to say, sulphur sulphodichloride, S<sup>2</sup>Cl<sup>2</sup>, saturated with chlorine at 10.8°, will contain 100 p.c. of sulphur dichloride.

Michaelis has also brought forward a considerable amount of chemical evidence tending to prove the existence of sulphur tetrachloride. Thus, if chlorine is passed into sulphur sulphodichloride cooled by a mixture of ice and salt, and after some time

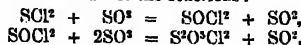
the refrigerating mixture is removed and displaced by ice, and sulphuric anhydride distilled into the chloride, the current of chlorine being maintained, an action takes place, only towards the close of which sulphurous anhydride is evolved. The product is a mixture of sulphurous (thionyl) and pyrosulphuric chlorides, formed in virtue of the reaction represented by the equation:



That the action does not take place in the following manner:



that is to say, that it is not the result of the reactions:



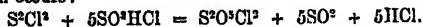
is proved by the fact, that sulphurous anhydride is evolved in small quantity only, and quite towards the end of the operation, and that the quantities of sulphurous and pyrosulphuric chlorides which are formed are in accordance with the first equation above given. The complete conversion of the  $\text{S}^2\text{Cl}^2$  into  $\text{SCl}^4$ , under these circumstances, is easily comprehended, although when saturated with chlorine at  $0^\circ$  it only contains about 9 p.c. of  $\text{SCl}^4$ , because as fast as this latter is acted upon by the anhydride, a fresh quantity is formed by the action of the chlorine, and thus ultimately the whole of the  $\text{S}^2\text{Cl}^2$  becomes  $\text{SCl}^4$ .

Pure sulphur tetrachloride is acted upon by sulphuric anhydride in the following manner:



which explains the evolution of sulphurous anhydride above spoken of; a small quantity of pyrosulphuric chloride is also produced by the action of the anhydride on the sulphurous chloride. Sulphuric chlorhydrate has a similar action at  $0^\circ$ , and higher temperatures, hydrochloric acid being also evolved; but at temperatures below  $0^\circ$  a solid body of the composition  $\text{S}^2\text{O}^3\text{Cl}^2$  is produced (p. 1132). Sulphur tetrachloride has no action on sulphurous anhydride.

On warming a mixture of sulphur sulphodichloride and sulphuric chlorhydrate, the following reaction occurs:

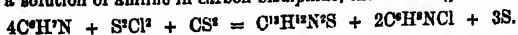


By heating phosphorous chloride with sulphur sulphodichloride to  $160^\circ$ , phosphoric chloride and phosphoric sulphochloride are produced:

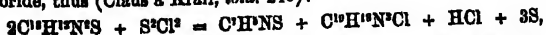


These two substances may be easily separated by distillation, and the reaction affords a convenient method of preparing pure phosphoric sulphochloride (Michaelis, *Zeitschr. f. Chem.* [2], vii. 152).

Sulphur sulphodichloride acts readily upon aniline: sulphur is separated, and aniline hydrochloride and a resinous substance are obtained; the latter appears to be a mixture of several colouring matters, the composition of which has not, however, been ascertained (Claus, *J. pr. Chem.* [2], iii. 256). When sulphur sulphodichloride is added to a solution of aniline in carbon bisulphide, the following reaction occurs:



If more than 1 mol. of sulphur chloride is employed, the sulphocarbaniide is converted into phenyl isosulphocyanate (phenylic mustard-oil) and triphenylguanidine hydrochloride, thus (Claus & Krall, *ibid.* 240):



the reaction being precisely similar to that which Hofmann has shown to occur with iodine.

#### OXYCHLORIDES OF SULPHUR.

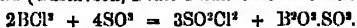
**Sulphurous Chloride,  $\text{SOCl}^2$ .** According to Michaelis (*Ann. Ch. Pharm.* clxx. 20), this compound is readily prepared by the action of sulphuric anhydride on sulphur tetrachloride:



It is easily separated by distillation from the small quantity of pyrochloride which is formed, and about 80 p.c. of the amount which theory indicates may be obtained in this way.

**Sulphuric Chloride,  $\text{SO}^2\text{Cl}^2$ .** Michaelis (*Zeitschr. f. Chem.* [2], vii. 149) has failed to obtain this compound by the action of phosphoric chloride on sulphuric anhydride, sulphuric chlorhydrate, and lead sulphate (v. 578), but he succeeded in preparing it by Regnault's method.

It is produced by heating sulphuric anhydride with boron chloride in sealed tubes to 120° for eight hours (Gustavson, *Deut. Chem. Ges. Ber.* vi. 9):



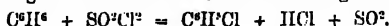
Gustavson did not succeed, however, in obtaining sulphuric bromide by employing boron bromide: the products in this case were sulphurous anhydride, bromine, and the compound of boric and sulphuric anhydrides.

Sulphurous chloride may be prepared by passing a mixture of sulphurous anhydride and chlorine over purified charcoal, or into glacial acetic acid. In the latter case, it is separated from the acid by distillation.

Sulphurous chloride is gradually acted upon by phosphoric chloride at the ordinary temperature (Michaelis):

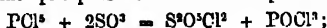


Benzene is not attacked by sulphurous chloride even at the boiling point of the mixture, but on heating in sealed tubes to 150° the following reaction occurs:

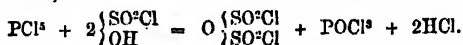


Similarly, phenol is converted into monochlorophenol, but the action takes place readily at ordinary temperatures (Dubois, *Zeitschr. f. Chem.* [2], ii. 705).

**Pyrosulphuric Chloride**,  $\text{S}^2\text{O}^2\text{Cl}^2$  or  $\text{ClO}^2\text{S}-\text{O}-\text{SO}^2\text{Cl}$ . This compound is produced on warming together phosphoric chloride and sulphuric anhydride:



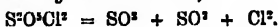
and by the action of phosphoric chloride on sulphuric chlorhydrate (Michaelis, *Zeitschr. f. Chem.* [2], vii. 149):



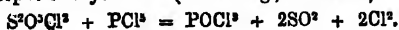
It is also formed by the action of sulphuric anhydride on sulphur sulphodichloride and sulphur tetrachloride (Michaelis), and on silicon tetrachloride (Gustavson), and by heating sulphuric anhydride with phosphoric oxychloride to 160° (Michaelis):



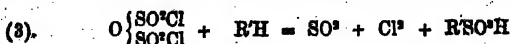
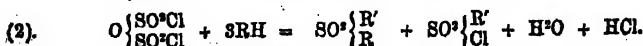
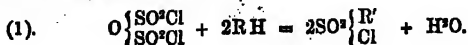
Pyrosulphuric chloride is a colourless, oily liquid of sp. gr. 1.819 at 18°, boiling at 146° (corr.) (Michaelis). In contact with water it decomposes slowly and noiselessly, and is thus distinguished from sulphuric chlorhydrate, which is rapidly decomposed with almost explosive violence when thrown into water. When heated above its boiling point, it is resolved into chlorine and sulphurous and sulphuric anhydrides (Armstrong, *Proc. Roy. Soc.* xviii. 511):



When submitted to the action of phosphoric chloride, it furnishes chlorine, sulphurous anhydride, and phosphoric oxychloride (Armstrong; Michaelis):



The hydrocarbons of the benzene series and their derivatives, the phenols, &c., are readily acted upon by pyrosulphuric chloride; the mode of action is represented by the following general equations:

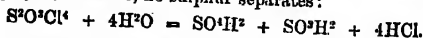


Chlorine, however, appears never to be evolved as such, but produces chlorinated compounds: phenol, for example, yields a mixture of chlorophenol and chlorophenol-sulphonic acids. The extent to which the reactions above formulated occur is found to vary with the conditions of experiment and the nature of the substance acted upon. Benzene, for example, yields all the possible products, whilst with the crystalline dibromobenzene the reaction is chiefly that represented by the first equation (Armstrong a. Pike, *Chem. News*, xlix. 283).

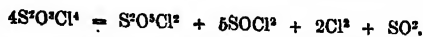
**Sulphur Oxytetrachloride**,  $\text{S}^2\text{O}^2\text{Cl}^4$  or  $\text{ClO}^2\text{S}-\text{O}-\text{SOCl}_2$ . To prepare this compound, which was first obtained by Millon by the action of moist chlorine on chloride of sulphur saturated with chlorine (*Ann. Ch. Phys.* [3], xlix. 237), a mixture of 1 mol. of sulphur sulphodichloride and 2 mols. of sulphuric chlorhydrate is introduced into

a capacious flask, surrounded by a mixture of ice and salt, and dry chlorine passed in through a wide tube. A considerable evolution of gas soon sets in, and a solid substance separates; the crust is broken from time to time with a glass rod, and when the whole is converted into solid, the flask is removed from the refrigerating mixture, and the current of chlorine continued until the reddish mass becomes colourless. This is facilitated by frequent shaking. The excess of chlorine is then displaced by a current of dry carbonic anhydride, and the product afterwards transferred to stoppered bottles. Any required quantity of the substance may in this way be prepared with the greatest readiness (Michaelis, *Ann. Ch. Pharm.* clxx, 22).

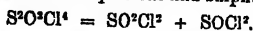
Sulphur oxytetrachloride is a white crystalline substance when pure, but is usually coloured yellow by adhering chlorine; it then closely resembles phosphoric chloride in appearance. It decomposes violently in contact with water, sulphurous, sulphuric, and hydrochloric acids being produced and sulphur separated; when a mixture of ice and water is employed, however, no sulphur separates:



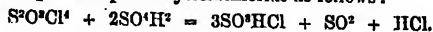
When exposed over water under a shade it gradually deliquesces, and chlorine, sulphurous anhydride, and hydrochloric acid are evolved; the liquid is a mixture of sulphurous and pyrosulphuric chlorides. When heated to  $57^{\circ}$  it melts with evolution of chlorine and sulphurous anhydride, but a portion sublimes in fine white needles; if the heating be continued, a liquid product is obtained, consisting of sulphurous and pyrosulphuric chlorides:



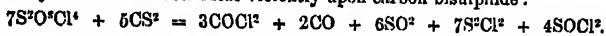
It is changed, after long keeping in sealed tubes, into a yellow liquid; this boils at  $73^{\circ}$ , and appears to be a mixture of sulphurous and sulphuric chlorides:



Sulphuric acid decomposes sulphur oxytetrachloride as follows:

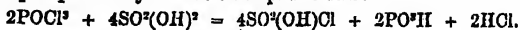


Sulphur oxytetrachloride acts most violently upon carbon bisulphide:

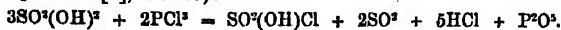


Alcohol also acts violently upon the chloride, ethyl chloride and sulphurous acid being evolved, but the nature of the remaining products has not been ascertained.

**Sulphuric Chlorhydrate,**  $SO^2HCl = SO^2\begin{smallmatrix} OH \\ Cl \end{smallmatrix}$ . The product obtained by the action of 1 mol. phosphoric chloride on 1 mol. sulphuric acid is a mixture of pyrosulphuric chloride and sulphuric chlorhydrate. Pure sulphuric chlorhydrate can be obtained by using the proportions recommended by Williams (1st *Suppl.* 1069), and by the action of phosphoric oxychloride on sulphuric acid:



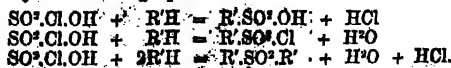
Also by warming a mixture of phosphorous chloride and sulphuric acid (Michaelis, *Zeitschrift. f. Chem.* [2], vii. 150):



It is advantageously prepared by slowly adding 1 mol. of phosphorous chloride to 3 mols. sulphuric through which a current of dry chlorine is passed; the flask containing the acid should be surrounded by cold water (Michaelis, *Ann. Ch. Pharm.* clxx, 24).

Sulphuric chlorhydrate is a colourless liquid, of sp. gr. 1.776 at  $18^{\circ}$ ; it boils at  $158.4$  (corr.) (Michaelis).

The action of sulphuric chlorhydrate on a number of hydrocarbons and derivatives of hydrocarbons of the benzene series has been examined by Armstrong and by Armstrong a. Pike (*Chem. Soc. J.* [2], ix. 173; *Chem. News*, xxix. 283). The action may take place as represented by the following equations:



It varies, however, both with the nature of the substance acted upon and the conditions of experiment. Thus when the chloride is added to well-cooled toluene, the product consists almost entirely of toluene-sulphonic acid; but if the temperature is allowed to rise during the reaction, less sulphonic acid is produced, and a considerable quantity of toluene-sulphonic chloride and toluene sulphone,  $(C^6H^5)SO^2$ , is obtained. When the toluene is added to the chloride without cooling, the proportion of the two latter products is still greater.

H. E. A.

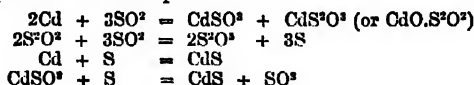
# 1134 SULPHUR: OXIDES AND OXYGEN-ACIDS.

**SULPHUR, OXIDES AND OXYGEN-ACIDS OF. I. Sulphurous Oxide, Acid, and Salts:** On the tension of sulphurous oxide at different temperatures, and its deviation from Boyle's law, see GASES (p. 547).

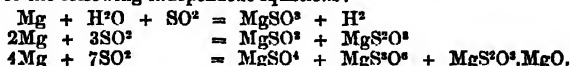
On its reaction with phosphorous chloride, see pp. 959, 960.

On its combination with tricalcio phosphate, see PHOSPHATES (p. 971); also *Chem. Soc. J.* [2], x. 39.

The action of sulphurous acid on certain metals has been studied by P. Schweizer (*Chem. News*, xxiii. 293). With zinc the products are hyposulphurous and trithionie acids and zinc sulphite, with separation of sulphur (compare 1st Suppl. 1063). With cadmium the products are sulphate, thiosulphate, dithionate, and sulphide, together with free sulphuric acid and sulphur:



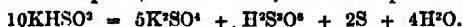
According to the last equation, sulphur in the nascent state should have the power of converting cadmium sulphite into cadmium sulphide and sulphuric anhydride. The action on nickel is similar, the first products being sulphite and thiosulphate of nickel, with a little free sulphur, afterwards sulphide and sulphate. On aluminium at ordinary temperatures and on magnesium at higher temperatures, sulphurous acid acts according to the following independent equations:



On the action of sulphurous acid on platine chloride, see PLATINUM (p. 985).

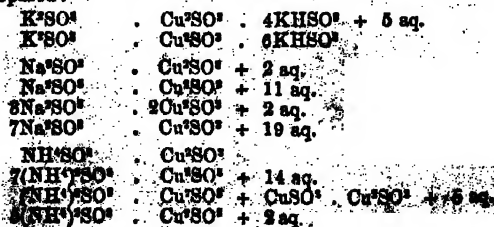
On the use of sulphurous acid in Bleaching, see F. Froesenius (*Chem. Centr.* 1871, 174; *Chem. Soc. J.* [2], ix. 452); in the Sugar manufacture: P. Schulze (*Dingl. pol. J.* cc. 231; *Jahresh. f. Chem.* 1871, 1082); in Brewing: Boanos (*Dingl. pol. J.* cxvii. 268; *Jahresh.* 1870, 1209).

**METALLIC SULPHITES. Spontaneous Decomposition.**—C. Saint Pierre (*Compt. rend.* lxii. 460; lxxiii. 749) finds that a dilute solution of acid potassium sulphite (prepared by treating 30 grams of carbonate with sulphurous acid, and diluting to 200 c.c.), heated in sealed tubes to 100°, and then left to itself for a long time (4 years), is resolved into sulphate, trithionic acid, and free sulphur:



A solution of acid lead sulphite kept for somewhat more than a year in sealed tubes at the atmospheric temperature was found to be completely decomposed, the whole of the lead being precipitated as sulphate, together with a little sulphur, while the solution contained free sulphuric acid, and another acid which gave a precipitate when warmed with a solution of cupric sulphate. From a solution of acid barium sulphite enclosed in sealed glass tubes, the whole of the barium was precipitated as sulphate after 10–12 hours heating in the water-bath. The solution still contained sulphurous acid, together with sulphuric acid, and an acid which formed black precipitates with mercury and silver salts. Liquid sulphurous oxide and the concentrated aqueous solution enclosed in glass tubes underwent no alteration either when heated in the water-bath for a month, or when kept at the atmospheric temperature for three years (Saint Pierre, *Compt. rend.* lxxiv. 52). At 170°–200°, however, aqueous sulphurous acid is resolved into sulphuric acid and free sulphur (Geitner, *Ann. Ch. Pharm.* cxxiv. 128; cxxix. 350; *Jahresh.* 1862, 69; 1864, 140).

**Copper Sulphites.**—These salts have been examined by N. Svenssen (*Deut. Chem. Ges. Ber.* iv. 713). The ordinary red salt is, as stated by Rammelsberg, a cuprous-cupric sulphite,  $\text{Cu}^2\text{SO}^3.\text{CuSO}^4 + 6\text{H}^2\text{O}$ . The simple cuprous sulphite,  $\text{Cu}^2\text{SO}^3$ , described by Rogojaki (v. 544), Svenssen was unable to obtain. The following double salts were prepared:



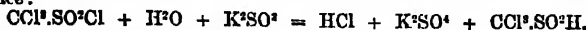
*Indium Sulphite*,  $2\text{In}^2\text{O}^3 \cdot 3\text{SO}^2 + 8\text{H}^2\text{O}$  (p. 680).

*Magnesium Sulphite*.—According to G. Archbold (*Pharm. J. Trans.* [3], ii. 844), the salt obtained by passing sulphurous oxide into water in which magnesium carbonate is suspended, crystallises in tetrahedrons, has the composition  $\text{Mg}(\text{SO}^2)^2 + 6\text{H}^2\text{O}$ , and gives off all its water at  $100^\circ$  (compare v. 546 and *Gmelin's Handbook*, iii. 235).

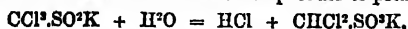
On the Sulphites of Platinum-bases, see pp. 993, 995, 996.

*Potassium Sulphite*.—On the spontaneous decomposition of acid potassium sulphite, see p. 1134.

The action of potassium sulphite on compounds containing the group  $\text{CCl}^3$  has been studied by Rathke (*Ann. Ch. Pharm.* clxi. 140). 1. When *trichloroformenesulphonic chloride*,  $\text{CCl}^3 \cdot \text{SO}^2\text{Cl}$ , is treated with a solution of neutral solution of potassium sulphite, the mixture becomes hot, sulphurous oxide is given off, and the following reaction takes place:



The easily decomposed potassium salt of the acid  $\text{CCl}^3 \cdot \text{SO}^2\text{H}$ , formed on neutralisation, cannot be separated out, but the presence of the acid is demonstrated by its peculiar penetrating odour, and by the immediate precipitation of trichlorosulphonic chloride on passing chlorine through the mixture. On boiling the solution of the potassium salt, it is converted into Kolbe's dichloroformenesulphonate of potassium:



*Potassium trichloroformenesulphonate*,  $\text{CCl}^3 \cdot \text{SO}^2\text{K}$ , mixed in solution with potassium sulphite, is first converted into the dichloroformenesulphonate, thus:

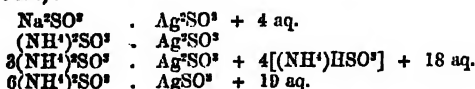


and then at temperatures above  $100^\circ$  into potassium formenedisulphonate (methionate), some potassium dithionate being also formed.

2. *Chloropicrin*,  $\text{CCl}^3\text{NO}^2$ , digested at a gentle heat with a solution of potassium sulphite, soon dissolves, producing potassium nitroformenedisulphonate,  $\text{CH}(\text{NO}^2)(\text{SO}^2\text{K})^2$ . This salt dissolves easily in hot, slowly in cold water; crystallises in spheroidal groups of microscopic plates, bears a tolerably high temperature without change, but detonates rather smartly at a stronger heat; gives precipitates with baryta-water and basic lead acetate, none with barium chloride, neutral lead acetate, silver nitrate, or mercurous nitrate.

3. The reactions of potassium sulphite with *trichloroacetic acid* and *chloral hydrate* have already been described (pp. 10, 309).

*Silver Sulphites*.—The following double sulphites of silver have been prepared by Stenksen (*loc. cit.*):



*Sodium Sulphites*.—According to Schultz-Sellack (*J. pr. Chem.* [2], ii. 459), neutral sodium sulphite,  $\text{Na}^2\text{SO}^3$ , crystallises with 7 mols.  $\text{H}^2\text{O}$ ; the deca-hydrated salt described by Muspratt (v. 550), Schultz-Sellack was unable to obtain. A supersaturated solution likewise yields the salt  $\text{Na}^2\text{SO}^3 + 7\text{H}^2\text{O}$ . Sodium sulphite has, like the sulphate, a maximum of solubility, and separates from warm solutions in the anhydrous state, as observed by Rammelsberg. This anhydrous salt is perfectly unalterable in the air, and when moistened with water cakes together, and is converted into the hydrate. From a solution containing a large excess of caustic soda it separates by evaporation in a vacuum at ordinary temperatures, in somewhat more distinct crystals. The *anhydrous sulphite*,  $\text{Na}^2\text{SO}^3$ , formed by supersaturating a concentrated solution of sodium carbonate with sulphurous acid, crystallises on cooling, and gradually gives off sulphurous oxide on exposure to the air.

II. *Sulphuric Oxide, Acid, and Salts*.—SULPHURIC OXIDE OR ANHYDRIDE,  $\text{SO}^3$ . The existence of two modifications of this body, first noticed by Marignac (v. 569) has been confirmed by Schultz-Sellack (*Pogg. Ann.* cxxxix. 480). *α-Sulphuric oxide*, formed on cooling the liquid oxide, solidifies at  $+16^\circ$  in long colourless prisms which melt at the same temperature; it boils at  $46^\circ$ ; vapour-tension at  $20^\circ$ , about 200 mm. *β-Sulphuric oxide* is produced from the *α*-modification at temperatures below  $25^\circ$ , above  $27^\circ$  the transformation does not go on. It forms extremely fine white needles; at temperatures above  $50^\circ$  it gradually liquefies and passes into the first modification; at ordinary temperatures it gradually forms vapours which have the constitution of the vapour of the first modification, and after remaining for a week in

a vacuum, at  $20^{\circ}$ , have a tension of 30–40<sup>2</sup> mm. The vapour, both of the solid and of the liquid oxide, exhibits the normal density, viz. 2.74 to 2.76 (calc. for  $\text{SO}^2 = 2.76$ ). The liquid oxide undergoes very great expansion by heat, its mean coefficient of expansion between  $25^{\circ}$  and  $45^{\circ}$  being 0.0027 for  $1^{\circ}$ , that is to say, more than two-thirds as great as that of gases. The two modifications also differ greatly in their relations to solvents. Liquid sulphuric oxide mixes in all proportions with hydrogen sulphate,  $\text{H}^2\text{SO}^4$ ; the  $\beta$ -oxide dissolves in sulphuric acid with extreme slowness, and gradually separates from a mixture of 10 pts.  $\text{SO}^2$  and 1–2 pts.  $\text{H}^2\text{SO}^4$ . With a larger proportion of the acid, no solid oxide separates, even on cooling to a low temperature; if the proportion of acid,  $\text{H}^2\text{SO}^4$ , amounts to 5 pts. for 10 pts. of oxide, the mixture may deposit crystals of pyrosulphuric acid,  $\text{H}^2\text{S}^2\text{O}^7$  or  $\text{H}^2\text{SO}^4.\text{SO}^2$ .

Liquid sulphuric oxide likewise mixes in all proportions with sulphurous oxide; if the latter is in excess, the mixture does not deposit anything solid, even when cooled to a low temperature. A mixture of equal parts of the two deposits on cooling  $\beta$ -sulphuric oxide, which redissolves at ordinary temperatures; if, on the other hand, the sulphuric oxide is in excess, part of the mixture solidifies even at ordinary temperatures. Sulphuric and sulphurous oxides do not appear to form a definite compound, as supposed by H. Rose (*Pogg. Ann.* xxxix. 173); nevertheless, the existence of a strong attraction between them may be inferred from the raising of the boiling point of the mixture. A mixture of the two oxides in equal parts boils at  $+5^{\circ}$ .

Carbon Sulphide mixes perfectly with liquid sulphuric oxide at  $30^{\circ}$ ; at  $15^{\circ}$  each of these liquids takes up only about  $\frac{1}{2}$  of the other. A mixture of the two in equal parts boils at  $34^{\circ}$ . They act chemically on one another, especially in presence of small quantities of sulphuric acid, the mixture after a while depositing a brown viscid mass. (Compare 1st. *Suppl.* p. 1067.)

**Reactions.**—Selenium exposed to the vapour of sulphuric oxide at ordinary temperatures is converted, first into a pasty mass, then into a yellow granular powder,  $\text{SeSO}^2$ , which, when gently heated, gives off sulphurous oxide and leaves selenium; it dissolves with yellow colour in sulphuric acid, the selenium being precipitated on dilution with water. Tellurium is almost completely oxidised by sulphuric oxide even at ordinary temperatures. Iodine exposed to the vapour of sulphuric oxide forms laminar crystals having nearly the composition  $\text{I}^2\text{SO}^2$ . Partial oxidation takes place, however, perhaps to periodic acid, and sulphurous oxide is evolved.

On the reaction of sulphuric oxide with phosphorous chloride, see p. 960.

The chlorides of the alkali-metals exposed to the long-continued action of sulphuric oxide vapour are converted into granulo-crystalline masses, having the composition  $\text{NaCl}(\text{SO}^2)^4$  and  $\text{KCl}(\text{SO}^2)^4$ . With silver chloride, a compound is formed having nearly the composition  $\text{AgCl}(\text{SO}^2)^4$ . Barium chloride yields the compound  $\text{BaCl}^2(\text{SO}^2)^3$ , which, when heated, first gives off  $\text{SO}^2$ , then chlorine and  $\text{SO}^2$ , leaving barium sulphate.

Sulphuric oxide is likewise absorbed by metallic fluorides, bromides and iodides, but in the two latter cases with decomposition, and separation of bromine or iodine. Mercuric cyanide absorbs sulphuric oxide, but likewise with partial decomposition. Potassium nitride appears to form with it the compound  $\text{KNOSO}^4$ , which, however, is more easily obtained by the action of liquid sulphurous oxide on potassium nitrate, with careful exclusion of water. The action of sulphuric oxide on saltpetre does not yield any compound analogous to the lead-chamber crystals,  $\text{HNO}^2\text{SO}^4$ .

When vapour of sulphuric oxide is passed slowly and with frequent agitation into strong nitric acid well cooled by water or ice, a thickish oily mass is obtained, which at a certain degree of concentration either deposits crystals or crystallises altogether. On dissolving this crystalline product in gently warmed dilute nitric acid, and draining the crystals which separate on cooling on a porous tile, they are obtained colourless and dry. Their analysis gives numbers leading to the empirical formula,  $48\text{O}^2.\text{N}^2\text{O}^3.3\text{H}^2\text{O}$ ; whence may be deduced the rational formula,  $\text{N}^2\text{O}^4.\text{SO}^2 + 3\text{SO}^2.\text{H}^2$ . The crystals are very deliquescent, and decompose when heated, giving off brown fumes and yielding a sublimate which exhibits the properties of the compound  $\text{N}^2\text{O}^4.\text{SO}^2$  (R. Weber, *Pogg. Ann.* cxliii. 602).

On Boric Anhydrosulphate, see Boxon (p. 208).

**Action of Water on the Lead-Chamber crystals.**—Rammelsberg (*Deut. Chem. Ges. Ber.* v. 310) reports experiments by Philipp, from which it appears that the products of this reaction are nitrogen dioxide, nitric acid and nitrous acid. The crystals contain 11.02 p.c. nitrogen; the decomposition by water gave 11.76 p.c.; viz. 2.67 as nitrogen dioxide, 1.65 as nitric acid, and 7.54 as nitrous acid. The nitrogen dioxide and nitric acid are formed by the action of water on the nitrous acid (in which form probably the whole of the nitrogen is present in the crystals). The crystals decomposed by a solution of potassium iodide yield 9 p.c. nitrogen—that is to say, nearly 3 $\frac{1}{2}$  times as much as when they are decomposed by water.



On the reaction of sulphuric oxide and fuming sulphuric acid with boric oxide, see BORON (p. 208).

**SULPHURIC ACID,  $H_2SO_4$ .** *Occurrence in Nature.*—In several localities near the Gulf of Mexico, small stagnant pools of water are found containing free sulphuric acid (1·529 gram in a litre). These waters likewise contain a large quantity of aluminium sulphate, together with iron sulphate, and most of them give off bubbles of hydrogen sulphide, marsh gas, and carbon dioxide. A petroleum spring occurs in the neighbourhood (J. W. Mallet, *Chem. News*, xxvi. 117).

On the Formation of Sulphuric acid in the Animal body, see E. Salkowski (*Deut. Chem. Ges. Ber.* v. 637; *Chem. Soc. J.* [2], x. 1033).

*Manufacture.*—On the Preparation of Sulphuric acid by the Roasting of Sulphuretted ores, see Hasenclever a. Helbig (*Dingl. pol. J.* cxcix. 284; *Chem. Centr.* 1871, 267; *Jahresb. f. Chem.* 1871, 981).

On the Concentration of Sulphuric acid, Stoddart (*Chem. News*, xxiii. 167; *Dingl. cc.* 419; *Jahresb.* 1010); Bode (*Dingl. cci.* 45; *Chem. News*, xxiv. 82; *Jahresb.* 1871, 1010); Galletly (*Chem. News*, xxiv. 106; *Dingl. cci.* 538; *Jahresb.* 1871, 1010); Hasenclever (*Deut. Chem. Ges. Ber.* v. 502; *Dingl. ccv.* 125; *Jahresb.* 1872, 973; *Chem. News*, xxvi. 174; *Chem. Soc. J.* [2], x. 929); De Hemptinne (*Dingl. ccv.* 419; *ccvi.* 155; *Jahresb.* 1872, 973).

On the recovery of Nitrous acid in Sulphuric acid works by the use of Glover's Towers, see G. Lunga (*Dingl. cci.* 341; *ccii.* 532; *Chem. Centr.* 1871, 618; *Jahresb.* 1871, 1011, 1014); F. Bode (*Dingl. ccii.* 448; *Jahresb.* 1871, 1013; *Chem. Soc. J.* [2], x. 1013).

*Thermic Relations.*—On the Specific Heat of Sulphuric acid and Sulphates in solution, see HEAT (pp. 597, 599, 601).

On the Density and Expansibility of the same solutions, p. 603.

On the Heat of Formation of Sulphuric acid and the other Oxygen-acids of Sulphur, pp. 609–611.

On the Heat of Combination of Sulphuric acid with Bases: Thomsen (*1st Suppl.* 683, 684, 1086); also Andrews (*Chem. Soc. J.* [2], viii. 432; *Jahresb.* 1870, 129); Bertholot (pp. 628–631 of this volume).

On the Heat of Combination of Sulphuric acid with Water, see p. 633 of this volume; also Thomsen (*Deut. Chem. Ges. Ber.* iii. 496; *Jahresb.* 1870, 127–129).

*Electrolysis.*—According to H. Highton (*Chem. News*, xxvi. 117), when dilute sulphuric acid is electrolysed, with zinc for the positive and charcoal for the negative electrode, hydrogen sulphide is evolved at the latter. That this gas does not proceed from pyrites mixed with the carbon is shown by the fact that its evolution ceases as soon as the circuit is broken.

On the Reduction of Sulphuric acid to Hydrogen Sulphide by the action of *Nascent Hydrogen*, see p. 658.

On the action of Sulphuric acid on Alcohol and Ether at high temperatures, see ETHYL ALCOHOL (p. 473).

**METALLIC SULPHATES.**—On the Decomposition (dissociation) of sulphates in solution, see CHEMICAL ACTION (pp. 292–304). On the Heat evolved or absorbed in their dissolution in water, pp. 292–298. On the Contraction attending dissolution, pp. 298–304. On the Freezing of sulphate solutions, p. 1070.

On the Electrolysis of sulphates, p. 460.

*Antimonious Sulphate,  $Sb_2(SO_4)_3$ ,* is obtained by evaporating a solution of antimonious oxide in moderately concentrated sulphuric acid, in long needles having a silky lustre. It is permanent in dry air, is decomposed by water, and gives off sulphuric oxide at a red heat (Schultz-Sellack, *Deut. Chem. Ges. Ber.* iv. 13).

*Barium Sulphate,  $BaSO_4$ .*—H. Struve (*Zeitschr. anal. Chem.* ix. 34) corroborates the fact observed by Schultz-Sellack (*1st Suppl.* 1070–1073) that the sulphates of barium, calcium, strontium, and lead dissolve in strong sulphuric acid, and separate from the solution in crystals on evaporation; he gives the following Table of solubilities:

	100 pts. of strong sulphuric acid dissolve	100 pts. of Nordhausen sulphuric acid dissolve
$BaSO_4$	5·69 pts.	15·80 pts.
$SrSO_4$	5·68	9·77
$CaSO_4$	2·03	10·17
$PbSO_4$	0·13	4·19

On the solubility of barium sulphate in water and hydrochloric acid, and on its precipitation in presence of other salts, see p. 1128.

**Bismuth Sulphates.**—According to Schultz-Sellack (*Deut. Chem. Ges. Ber.* iv. 13), the normal salt,  $\text{Bi}(\text{SO}_4)^3$ , is easily obtained by evaporating a solution of bismuth oxide in moderately strong sulphuric acid, and forms slender needles which may be heated nearly to redness without decomposition. According to A. Leist, on the other hand (*Ann. Ch. Pharm.* clx. 29), the salt formed by dissolving bismuth oxide in sulphuric acid is not a neutral, but a mixture of an acid salt,  $\text{Bi}^2\text{O}^3 \cdot 4\text{SO}^3 + 7\text{H}^2\text{O}$  (or  $+ 9\text{H}^2\text{O}$ , according to the concentration of the sulphuric acid, from which the salt has crystallised) =  $\text{BiH}(\text{SO}_4)^2 + 3\text{H}^2\text{O}$ , with a basic salt,  $\text{Bi}^2\text{O}^3 \cdot 2\text{SO}^3 + 2\text{H}^2\text{O}$ , agreeing with Heintz's sesquibasic sulphate (v. 584), excepting that it contains 1 mol. water less. The acid salt is obtained by dissolving bismuth oxide in moderately dilute sulphuric acid (1 pt.  $\text{H}^2\text{SO}_4$  to 2 or 3 pts.  $\text{H}^2\text{O}$ ), redissolving the basic salt which separates in a large quantity of sulphuric acid (about 1 pound of strong sulphuric acid to 15 grams of bismuth oxide), then filtering and evaporating. The acid salt then separates in long shining needles which may be freed from mother-liquor by spreading them on a tile and pressing them between bibulous paper. It is insoluble in water, but dissolves in acids, especially in hydrochloric and nitric acids. When washed for several days with hot water, and then carefully dried by pressure for a week between bibulous paper, it was converted into a salt having the composition  $4\text{Bi}^2\text{O}^3 \cdot 3\text{SO}^3 + 15\text{H}^2\text{O}$ . The basic salt,  $\text{Bi}^2\text{O}^3 \cdot 2\text{SO}^3 + 2\text{H}^2\text{O}$ , is obtained by dissolving bismuth oxide in sulphuric acid diluted as above, filtering from separated salt, and evaporating. The crystals are likewise needle-shaped, but not so long as those of the acid salt (Leist).

**Cadmium Sulphate.**—This salt, subjected for several hours to the action of a stream of ammonia gas, falls to powder and is converted into the ammonio-salt,  $\text{CdSO}_4 \cdot 6\text{NH}_3$ , the ammonia in which exhibits the following tensions:

Temperature Tension in millimeters of mercury	48°5'	51°5'	100°	100°	100°	100°	100°	100°
	368	439	1374	1364	1366	1364	1361	1365

The compound left after heating to 100° is  $\text{CdSO}_4 \cdot 2\text{NH}_3$ . These ammonia-compounds, like all others of the same class in the pulverulent form, absorb ammonia mechanically like charcoal, the tension of the gas at any given temperature being variable up to the point at which the salt retains only combined ammonia (Isambert, *Compt. rend.* lxx. 456). Compare 1st Suppl. p. 426.

**Cerium Sulphates.** See CERIUM (p. 275).

**Glucinum Sulphate,**  $\text{GSO}_4 + 4\text{H}^2\text{O}$ , crystallises in the quadratic system. Axes  $a : c = 1 : 0.9461$ . Observed forms, 011 (110), or  $\text{P}^\infty \cdot \infty \text{P}$ . Sp. gr. of the crystals = 1.725 (Topsøe, *Wien. Acad. Ber.* [2 abth.] lxxvi. 5).

**Gold Sulphates** (p. 576).

**Iron Sulphates.**—H. Rheinock (*Dingl. pol. J.* cclii. 268; *Chem. Soc. J.* [2], x. 225) infers from experiments of his own that ammonio-ferrous sulphate and potassio-ferrous sulphate crystallise, not with 6 mols. water, as commonly supposed, but with 5 mols. According to E. Fleischer, on the other hand (*J. pr. Chem.* [2], v. 437; *Chem. Soc. J.* [2], x. 1079), the ammonio-ferrous salt has the formula commonly assigned to it, viz.:  $\text{Fe}(\text{NH}_4)(\text{SO}_4)^2 + 6\text{H}^2\text{O}$ .

**Lead Sulphate,**  $\text{PbSO}_4$ .—On the solubility of this salt in strong sulphuric acid, see p. 1137. On its solubility in various salts of organic acids in presence of alcohol, see F. H. Storer (*Chem. News*, xxi. 17; *Jahresb.* 1870, 356).

**Magnesium Sulphates.**—**Ammonium-magnesium sulphate,**  $(\text{NH}_4)^2\text{SO}_4 \cdot \text{MgSO}_4 + 6\text{H}^2\text{O}$ , has been found by O. Popp (*Ann. Ch. Pharm.*, Suppl. viii. 1) in the boric acid lagunes of Tuscany, especially in those at Sasso and Acquaviva, which are poorest in boric acid. In the salt from these two localities, not purified by recrystallisation, the magnesia is replaced in variable proportions by manganous and ferrous oxides, and lime appears also to be present as an amorphous constituent. The mother-liquors which remain after the crystallisation of the boric acid contain small quantities of potassium-magnesium sulphate. Popp designates all the isomorphous double sulphates of the magnesia group occurring in the fumaroles of Tuscany as 'Carbolites.'

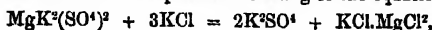
A solution of 1 mol. potassium chloride and 1 mol. magnesium sulphate deposits, on evaporation, the double salt,  $\text{K}^2\text{SO}_4 \cdot \text{MgSO}_4 + 6\text{H}^2\text{O}$ , which, when treated with a quantity of water not sufficient to dissolve it completely, leaves a residue of pure potassium sulphate, while the solution deposits first the double salt above mentioned, and then the salt  $\text{K}^2\text{SO}_4 \cdot 2\text{MgSO}_4 + 14\text{H}^2\text{O}$ . The mother-liquor decanted from the first salt yields, by further concentration, a crop of crystals which, when dried upon a tile, have the composition  $2\text{K}^2\text{SO}_4 \cdot 4\text{KCl} \cdot \text{MgCl}_2 + 7\text{H}^2\text{O}$  or  $\text{K}^2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{KCl} + 7\text{H}^2\text{O}$ .

The following crystallisations consist chiefly of potassium-magnesium chloride, and the last mother-liquors contain almost pure magnesium chloride.

**Molybdenum Sulphates.**—*Neutral molybdic sulphate*,  $(\text{MoO})^2\text{SO}_4$ , separates, according to Schultz-Sellack (*Deut. Chem. Ges. Ber.* iv, 13), from a solution of the trioxide in moderately strong sulphuric acid, in colourless shining crystals which deliquesce on exposure to the air, and turn blue in consequence of the reducing action of particles of dust. When heated they easily decompose, and give off sulphuric oxide. The aqueous solution dries up to a horny mass. The salt,  $\text{Mo}^2(\text{SO}_4)^2$ , described by Anderson (v. 605), Schultz-Sellack was unable to obtain.

**Platinum Sulphates, Ammoniacal** (pp. 994–1003).

**Potassium Sulphate**,  $\text{K}^2\text{SO}_4$ .—H. Grüneberg (*Chem. Centr.* 1870, 623) prepares this salt by decomposing native potassium-magnesium sulphate (schönite) with potassium chloride. The reaction would proceed according to the equation:



were it not that the carnallite (or magnesium chloride) produced interferes with the complete action of the salts on one another. The saturated solution (27° B.) of 2 mols. schönite is added at the boiling heat to 3 mols. of finely powdered crystallised potassium chloride. The latter is quickly converted into sulphate, but as soon as the temperature of the solution falls below 40°, chloride of potassium again separates out. To prevent this, the lye must be decanted from the potassium sulphate while at 40°. On evaporating this liquid, potassium sulphate crystallises out first, then schönite, and lastly carnallite. The potassium sulphate may be easily brought to 95 p.c. by centrifugalising and covering it with a small quantity of water.

Schönite may also be decomposed by niterating it several times with a cold saturated solution of pure potassium chloride (21° B.)

To purify the crude commercial potassium sulphate (*plate sulphate of potash*), which usually has the composition  $3\text{K}^2\text{SO}_4 \cdot \text{Na}^2\text{SO}_4$  (vi. 609), Sonstadt (*Chem. News*, xxvi. 195) boils the aqueous solution with potassium chloride. The hot solution on cooling deposits pure chloride of potassium, the sodium chloride remaining dissolved. This 'plate sulphate' does not appear to be a true double salt, as its composition is not constant. A well-crystallised sample was found by J. Mahony (*ibid.* xxii. 217) to contain 77.60 p.c.  $\text{K}^2\text{SO}_4$  (calc. 78.56).

On the reaction of potassium sulphate with *gypsum*, see p. 589.

**Silver Sulphate.**—On the reactions of this salt with *iodoform*, *chloroacetic acid*, *chlorobenzoic acid*, and *ethyl iodide*, see Kämmerer (*Deut. Chem. Ges. Ber.* iv, 219; *Jahresb.* 1871, 654; *Chem. Soc. J.* [2], 552).

**Sodium Sulphate**,  $\text{Na}^2\text{SO}_4$ .—*Crystallisation.*—According to Schultz-Sellack (*J. pr. Chem.* [2], ii. 459) a solution of this salt mixed with a large quantity of caustic soda deposits it at ordinary temperatures in the anhydrous state.

The spontaneous crystallisation of sodium sulphate from supersaturated solutions has been studied by De Coppet (*Bull. Soc. Chim.* [2], xvii. 146–155). His experiments confirm the statement of Loewel (v. 613), that the crystallising temperature of the heptahydrate,  $\text{Na}^2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , is for the most part higher as the solution is more concentrated; there is, however, no definite relation between the concentration and the depression of the crystallising point below the temperature of normal saturation. For a solution of given strength the crystallising point may vary by several degrees. According to existing observations the lowering of the crystallising temperature amounts to at least 7°, and mostly to about 12° for solutions containing from 20 to 35 pts. of anhydrous salt to 100 pts. water. With regard to the crystallisation of the decahydrate,  $\text{Na}^2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , De Coppet infers from his experiments that it is higher when the solution is quickly cooled. The presence of crystals of the heptahydrate exerts no perceptible influence on the crystallising temperature of the decahydrate. The influence of concentration is likewise almost imperceptible. At all events, the crystallisation of the decahydrate does not always take place exactly at  $-8^\circ$  to  $-7^\circ$ , as stated by Violette and Baumhauer. The point at which crystallisation begins is not regulated by any definite law. The first crystal forms sometimes on the side of the vessel, sometimes at the surface or in the interior of the liquid. In general a saline solution crystallises more readily the larger its quantity.

From his numerous observations on the freezing of saline solutions (pp. 1068–1071) De Coppet infers that the 'new hydrate' of sodium sulphate said by Tomlinson (*Proc. Roy. Soc.* xx. 109; *Chem. Soc. J.* [2], 4, 284) to crystallise at or below  $-3.3^\circ$ , and by Violette (*Études sur la Crystallisation*, Paris, 1867) at  $-4^\circ$ , is nothing but a mixture of ice and the hydrate,  $\text{Na}^2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . According to De Coppet, sodium sulphate is at present known in four states, viz.: two modifications of the anhydrous salt, one separating below and the other above  $33^\circ$ , and the two hydrates with 7 and 10 mols.

H<sup>2</sup>O (*Compt. rend.* lxxiii. 1324; *Chem. News*, xxiii. 266; xxv. 102; *Chem. Soc. J.* [2], x. 284, 465). See also Liversidge (*Proc. Roy. Soc.* xx. 497-507).

On the *Specific Heat*, and *Density*, and *Expansion-coefficient* of aqueous sodium sulphate, see *HEAT* (pp. 599, 601, 603).

*Strontium Sulphate*, CrSO<sup>4</sup>.—On the solubility of this salt in sulphuric acid, see p. 1137.

*Uranium Sulphates*.—Normal uranic sulphate, (UO<sup>2</sup>)<sup>2</sup>SO<sup>4</sup>, [U = 240], separates on evaporation from solution in strong sulphuric acid, in honey-yellow, non-fluorescent crystals. It is not decomposed at a low red heat. It dissolves abundantly, though slowly, in water, and gradually absorbs water from the air. By dissolving it in not quite concentrated sulphuric acid and slowly evaporating the solution in an open dish at 200°, an acid sulphate, H<sup>2</sup>(UO<sup>2</sup>)(SO<sup>4</sup>)<sup>2</sup>, analogous in composition to the lead-chamber crystals, is obtained in fluorescent crystals of a fine yellow-green colour, which quickly deliquesce on exposure to the air. On mixing the solution of the normal sulphate in strong sulphuric acid with liquid sulphuric anhydride, the anhydrosulphate, (UO<sup>2</sup>)SO<sup>4</sup>.SO<sup>3</sup>, separates gradually in small yellow crystals. On heating the solution the salt separates immediately, but it is then generally mixed with the ordinary acid salt. It hisses when thrown into water (Schultz-Sellack, *Deut. Chem. Ges. Ber.* iv. 13).

### III. Disulphuric, Pyrosulphuric, or Anhydrosulphuric Acid, SO<sup>2</sup>(OH)

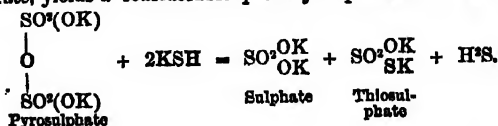


*Nordhausen Sulphuric acid* (v. 574).—Several salts of this acid

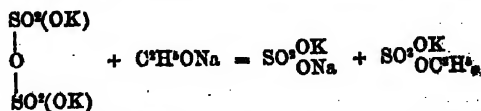
have been examined by Schultz-Sellack (*Deut. Chem. Ges. Ber.* iv. 109). The acid itself is easily obtained of definite composition by mixing sulphuric acid with the liquid anhydride, using a slight excess of the latter, and spreading the resulting crystals under a bell-jar over not quite concentrated sulphuric acid, which then takes up the excess of the anhydride. If the mixture contains a large excess of the anhydride, it remains fluid for a long time, and on cooling yields a deposit partly consisting of the β-anhydride (p. 1135). The dry crystals melt at 35°, and exhibit no vapour-tension. The acid mixes with sulphurous anhydride, which can then be expelled only by prolonged boiling.

The pyrosulphates of potassium and sodium have been known for some time (v. 608, 612). The *neutral potassium salt*, K<sup>2</sup>S<sup>2</sup>O<sup>7</sup>, prepared by the action of sulphuric anhydride on the heated normal sulphate, melts, according to Jacquelin, at 210°, according to Schultz-Sellack at 300°, and cannot be recrystallised. By dissolving it in strong, fuming sulphuric acid, it is converted into *hydropotassic pyrosulphate*, KHS<sup>2</sup>O<sup>7</sup>, which crystallises in transparent prisms melting at 168°. The salts, Na<sup>2</sup>S<sup>2</sup>O<sup>7</sup>, Ag<sup>2</sup>S<sup>2</sup>O<sup>7</sup>, and BaS<sup>2</sup>O<sup>7</sup>, prepared like the potassium salt, form colourless crystals. The barium salt hisses when thrown into water; it does not melt when heated, but decomposes at an incipient red heat (Schultz-Sellack).

Potassium pyrosulphate in fine powder, heated with an alcoholic solution of potassium sulphhydrate, yields a considerable quantity of potassium thiosulphate:

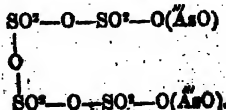


The same salt, boiled with alcoholic sodium ethylate, yields potassium ethylsulphate:



(Drechsel, *J. pr. Chem.* [2], v. 367).

An *arsenious anhydrosulphate*, As<sup>2</sup>(SO<sup>3</sup>)<sup>2</sup>SO<sup>3</sup>, which may perhaps be represented by the constitutional formula:



separates from a solution of arsenious oxide in fuming sulphuric acid, in slender shining needles, which are decomposed by water. The corresponding *antimony-compound*, first obtained by Peligot (v. 584), may be prepared in a similar manner (Schultz-Sellack).

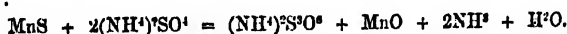
IV. **Iodosulphuric Acid**,  $\text{H}^2\text{SO}^3\text{I}^2$  (p. 684).

V. **Thiosulphuric Acid**,  $\text{H}^2\text{S}^2\text{O}^3 = \text{SO}^2 \begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$ . The salts of this acid have been examined by E. A. Letts (*Chem. Soc. J.* [2], viii. 424), who infers that they do not contain hydrogen as an essential constituent. He finds that the sodium salt,  $\text{Na}^2\text{S}^2\text{O}^3 \cdot 6\text{H}^2\text{O}$ , gives off the whole of its water at  $100^\circ$ , or in a vacuum over sulphuric acid; whereas, according to Papo (*1st Suppl.* 1073), a temperature of  $215^\circ$  is required to expel the last molecule of water. The *barium salt* crystallises with only one molecule of water, which is likewise expelled at  $100^\circ$ . The *lead salt*,  $\text{PbS}^2\text{O}^3$ , is anhydrous, as previously shown by Papo. The *strontium salt* appears to contain 5 mols. water, four of which are given off at  $100^\circ$ ; whereas at  $200^\circ$  only  $\frac{1}{2}$  mol.  $\text{H}^2\text{O}$  is expelled: hence Letts infers that the formula of the salt is  $2\text{SrS}^2\text{O}^3 \cdot 10\text{H}^2\text{O}$ , and that only 2 mols. of the water can be driven off without decomposition. The *magnesium salt*,  $\text{MgS}^2\text{O}^3 \cdot 6\text{H}^2\text{O}$ , gives off only 3 mols. water at  $100^\circ$ , the other three appearing to be retained till decomposition begins. The thiosulphates of *cobalt* and *nickel* contain 6 mols. water, and are easily decomposed.

*Lead thiosulphate* (1 mol.), treated with phosphorus pentachloride, yields, together with lead chloride, hydrogen chloride and sulphurous oxide, a distillate containing thionyl chloride,  $\text{SOCl}^2$ , phosphorus oxychloride, and probably also phosphorus phosphochloride. The reaction begins spontaneously, but requires heat to complete it (J. Y. Buchanan, *Deut. Chem. Ges. Ber.* iii. 485).

VI. **Dithionic Acid**. On the crystalline form of lead thionate, see Brezina (*Jahrbuch. f. Mineralogie*, iv. 642).

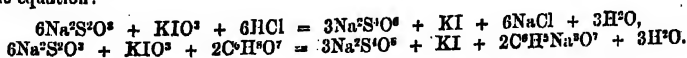
VII. **Trithionic Acid**,  $\text{H}^2\text{S}^3\text{O}^4$ . Ammonium trithionate is formed, with evolution of hydrogen sulphide and ammonia, by the action of ammonium sulphate on manganous sulphide:



The hydrogen sulphide probably results from the decomposition of part of the trithionate:  $(\text{NH}^4)^2\text{S}^3\text{O}^4 = 2\text{SO}^2 + (\text{NH}^4)^2\text{S}$ . (F. Muck, *Deut. Chem. Ges. Ber.* iv. 146).

*Potassium Selenio-trithionate*,  $\text{K}^2\text{SeS}^3\text{O}^4$ , forms monoclinic crystals exhibiting the faces  $\infty\text{P}$ ,  $\infty\text{P}'$ ,  $\infty\text{P}''$ ,  $\text{P}$ ,  $\text{P}'$ ,  $\text{P}''$ ,  $\text{oP}$ . Angle  $\infty\text{P} : \infty\text{P}' = 112^\circ 42'$ ;  $\infty\text{P}' : \text{P}' = 142^\circ 6'$ ;  $\text{P}' : \text{P} = 98^\circ 22'$  (B. Rathke, *J. pr. Chem.* [2] i. 33).

VIII. **Tetrathionic Acid**,  $\text{H}^2\text{S}^4\text{O}^6$ . When a mixed solution of a thiosulphate and iodate is treated with an acid, tetrathionate and iodate are produced, as shown by the equation:



**SUPERPHOSPHATES, ANALYSIS OF.** See PHOSPHATES (p. 970).

**SUPERSATURATED SOLUTIONS.** See SALINE SOLUTIONS (p. 1070).

**SURFACE-TENSION OF LIQUIDS.** See CAPILLARITY (p. 247).

**SYMPHYTUM.** The prickly comfrey (*S. aspernum*), a native of the Caucasus, is cultivated in some parts of Ireland as food for dairy-stock. The plant is perennial, is easily propagated by cuttings from the root, and yields a heavy crop. The ordinary produce is about 30 tons per acre, in several cuttings, but 82 tons has been reached. Analysis of plants grown in Oxfordshire gave the following results:—

	Natural state	Dried at $100^\circ$
Water	90.66	—
Oil and chlorophyll	0.20	2.20
Soluble nitrogenous compounds	1.10	11.81
Insoluble nitrogenous compounds	1.62	17.31
Gum, mucilage, and a little sugar	1.28	13.65
Woody fibre	3.30	35.43
Soluble mineral matters	1.25	13.32
Insoluble mineral matters	0.69	6.28
	100.00	100.00
Total nitrogen	0.434	4.66

Judging from its composition, the plant will have about the same feeding value as green mustard, turnip-tops, or Italian rye-grass grown on irrigated land (A. Voelcker, *Journ. Roy. Agr. Soc.* [2], vii. 387).

**SYNANTHROSE**,  $C^{12}H^{22}O^{11}$ . A sugar isomeric with cane-sugar, occurring, together with inulin, in the tuber-bearing *Compositæ* (see SUGARS (p. 1109)).

**SYNGENITE**. Potassio-calcic sulphate from the salt-beds of Kalusz in Galicia, Zepharovich (*Jahrb. f. Min.* 1872, 536) gave the name *syngenite* to a mineral of this composition, which he supposed to be rhombic, and J. Rumpf (*Min. Mitth.* 1872, 120) designated a monoclinic mineral of the same composition as *kalusite*. Subsequent investigation (*ibid.* 1873, 88, 638) having shown, however, that both minerals are monoclinic, and identical in form and composition with artificially prepared potassio-calcic sulphate,  $K^2SO^4 \cdot CaSO^4 + H^2O$ , the name *kalusite* has been dropped.

The first four of the following analyses (made on specimens originally called *kalusite*) are by Ullik (*Min. Mitth.* 1872, 120), the fifth by O. Völker (*Jahrb. f. Min.* 1873, 88). No. VI. gives the values calculated from the formula above given:

	I.	II.	III.	IV.	V.	VI. (calc.)
CaO . . .	17·24	17·09	16·67	16·62	16·97	17·06
MgO . . .	—	—	—	—	0·16	—
K <sup>2</sup> O . . .	28·67	28·53	28·40	28·72	28·03	28·70
SO <sup>2</sup> . . .	—	48·63	48·33	48·35	40·04	48·75
H <sup>2</sup> O . . .	5·50	5·46	5·46	5·45	5·81	5·18
Sp. gr. . . .	2·53 to 2·55				22·5	

The axial elements are:

Clinodagonal	Orthodagonal	Principal axis	
1·3801	: 1	: 0·8667	Rumpf
1·3699	: 1	: 0·8738	Zepharovich.

Angle of inclined axes 76° 9' (Rumpf); 76° 0' (Zepharovich).

## T

**TACHYLITE**. On the tachylite and dolerite of the Sababerg in Hesse, see **DOLERITE** (p. 439).

**TADJERITE**. The name given by Mounier to the rock composing the meteorite which fell at Tadjéra, near Setif, on June 9, 1867. On the black colouring matter of this rock, see Mounier (*Compt. rend.* lxii. 393; *Chem. Soc. J.* [2], ix. 329). On the conversion of serpentine into tadjerite: *Compt. rend.* lxxii. 541; *Chem. Soc. J.* [2], ix. 505.

**TALCOSITE**. A mineral from Victoria, where it occurs in thin laminar veins traversing selwynite. It feels like talc, has a silver-white colour, with a tinge of green or yellow and a nacreous lustre. The laminae are flexible and unelastic. Before the blow-pipe it becomes quite white, exfoliates, gives off water, and melts to a blistered enamel. Hardness = 1; at right angles to the lamination, = 1·5 to 2·0. Sp. gr. = 2·46 to 2·5 (Ulrich, *Silk. Am. J.* [2], i. 272). C. Newbery found, as the mean of two analyses, 40·04 p.c.  $SiO^2$ , 45·98  $Al^2O^3$ , and 4·80  $H^2O$ , with traces of chromic, ferrous, and manganous oxides.

**TAMMITE**. This name is proposed by Crookes for a mineral of unknown origin, analysed by H. Tamm (*Chem. News*, xxvi. 13). It has a specific gravity of 12·5 and contains 88·05 p.c. tungsten, 5·60 iron, 0·15 manganese, and 6·20 undetermined substance, said to contain neither oxygen nor sulphur.

**TAMPICIN**,  $C^8H^{14}O^{14}$  (Spirgatis, *N. Rep. Pharm.* xix. 452). A neutral substance resembling convolvulin, existing in *Tampico Jalap*. The tubers having been exhausted with water, the resin is extracted with alcohol, purified by boiling with water, and decolorised in alcoholic solution with animal charcoal. It dissolves in alcohol and in ether, and when treated with strong bases takes up  $3H^2O$ , and is con-

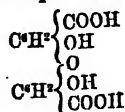
verted into tannic acid,  $C^{12}H^{10}O^8$ . This acid is amorphous, hygroscopic, easily soluble in water and in alcohol; neutral lead acetate and mercuric chloride, added to its solution, produce white clouds; basic lead acetate, a bulky precipitate.

Tampicin is resolved, by digestion with dilute acids, into sugar and tannic acid,  $C^{12}H^{10}O^8$ , which crystallises in slender needles, melts when heated to a faintly yellowish liquid, forms soluble salts with alkalis, insoluble salts with the earths and heavy metallic oxides.

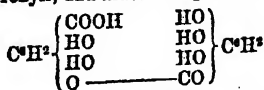
The medicinal action of tampicin resembles that of convolvulin.

**TANNIC ACID** and **TANNIN**. The nature and constitution of tannic acid from nut-galls (gallotannic acid) have been investigated by H. Schiff (*Deut. Chem. Ges. Ber.* iv. 231, 967; further, *Bull. Soc. Chim.* [2], xviii. 23). There is no doubt that crude tannic acid contains glucose, and that this substance is not merely mechanically retained in it; the percentage of sugar, however, has been very variously estimated by different observers, and it has been found possible, by appropriate treatment, to reduce the amount to a small percentage, the tannic acid thus purified exhibiting precisely the same properties as before. It has, therefore, long been a matter of dispute whether tannic acid was to be considered as a glucoside or not. The following experiments throw important light on the subject.

Well-purified crystallised tannic acid, dried at  $110^\circ$ , was mixed with phosphorus oxychloride to the consistence of an emulsion, and the mixture heated, first at  $100^\circ$ , afterwards at  $120^\circ$ , whereupon much hydrochloric acid was evolved, and the tannic acid was finally converted into a yellow powder which was washed several times by decantation with dry ether, and the residue, freed from ether by gentle warming, was dissolved in a small quantity of water. At the end of twelve hours a crystallisation of unchanged tannic acid (about 10 per cent.) was obtained. On saturating the yellow-red mother-liquor with salt, the whole solidified; and on the addition of more salt, the precipitate caked together to a resinous mass, from which the greater part of the salt-solution could be poured off. After twice washing with salt-solution, the resinous cake was dried in a vacuum, dissolved in absolute alcohol, and a considerable volume of ether was added to the solution, which was then filtered; after distilling off the ether, the mass was dried in a vacuum. The varnish-like slightly coloured residue thus obtained exhibits the reactions, solubility, physical properties, taste, &c., characteristic of tannic acid. It is the first tannic acid which has been prepared perfectly free from sugar. By heating with hydrochloric acid it was entirely converted into crystalline gallic acid, and this again into tannic acid. Analyses of various portions gave 51.7 to 52.3 per cent. C, and 3.4 to 4.1 per cent. H, agreeing with the formula  $C^{12}H^{10}O^8$ , which is that of an anhydride of digallic acid:  $C^{12}H^{12}O^{10} - H^2O = C^{12}H^{10}O^8$ . The tannic acid thus prepared is converted, by the action of acetic anhydride, into an acetyl-derivative which Schiff formerly supposed to be tetracetyl-tannic acid, whence he was led to regard tannic acid as an alcoholic anhydride of digallic acid containing four OH groups, and represented by the formula:



Subsequent experiments, however, have shown that this supposed tetracetyl-derivative is really a pentacetyl-tannic acid, whence it follows that the molecule of tannic acid must contain five hydroxyls, and must be represented by the formula:

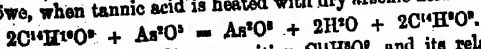


which is that of an etherated anhydride of digallic acid.

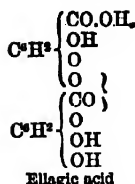
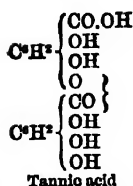
**Ellagic Acid**,  $C^{12}H^6O^8$ .—This acid is formed, according to Griessmayer (*loc. cit.*), by the action of iodine on tannic acid:



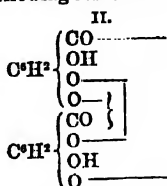
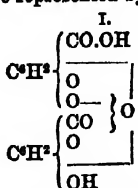
It is also formed in small quantity by the action of phosphorus oxychloride on tannic acid, or of the pentachloride on gallic acid, and when acetyl-tannic acid is boiled with magnesia and water, and the product is exposed to the air (Schiff); moreover, as observed by Löwe, when tannic acid is heated with dry arsenic acid:



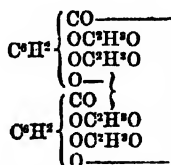
Ellagic acid dried at  $110^\circ$  has the composition  $C^{12}H^6O^8$ , and its relation to tannic acid may be represented as follows:—



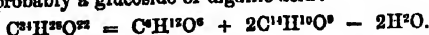
Air-dried ellagic acid,  $\text{C}^{14}\text{H}^8\text{O}^8 + \text{H}_2\text{O}$ , loses its water at  $100^\circ$ , but re-absorbs it from moist air. When it is heated to  $200^\circ$ – $210^\circ$ , the compound  $\text{C}^{14}\text{H}^8\text{O}^8$  is obtained, and this compound does not recover its water from moist air, but ebullition with water slowly reconverts it into ellagic acid. Consequently it is an anhydride of ellagic acid, and may be represented by one of the following formulae:—



The action of acetic anhydride on ellagic acid (dried at  $100^\circ$ ) gives rise to the formation of *tetracetyl-ellagic anhydride*. This compound forms a yellow crystalline powder, slightly soluble in water, alcohol or ether, and dissolving in sulphuric acid with the production of a yellow colour. Its constitution may, perhaps, be represented by the formula:



**Natural Tannin.** The above investigations prove that natural tannin is not a glucoside of gallic acid, and Schiff finds that pure pentacetyl-tannic acid may be obtained by the action of acetic anhydride on natural tannin, any glucose present being acetylated and subsequently removed by the action of water. That the glucose present in imperfectly purified natural tannin does not exist in the free state, is proved by the fact that ether-alcohol and anhydrous alcohol dissolve such tannin freely. Unaltered natural tannin is probably a glucoside of digallic acid:



This formula corresponds with 23 p.c. of glucose, and the amount of this substance obtained from natural tannin varies from 0 to 22 p.c., according to the extent to which the tannin has been purified. Schiff proposes to confine the term tannin to the glucoside, and to use the term *digallic acid* instead of tannic acid for indicating the product which yields no sugar (Schiff).

J. Löwe (*Zeitschr. anal. Chem.* 1872, 365; *Chem. Soc. J.* [2], xi. 748) also finds that pure gallotannic acid is not a glucoside, and that when dried at  $140^\circ$ – $145^\circ$  it has the composition  $\text{C}^{14}\text{H}^{10}\text{O}^8$ .

Gallotannic acid is not found in oak-bark, catechu, or other materials used in tanning. Even the tannin of the sumach exhibits different properties, and its analysis leads to the formula  $\text{C}^{16}\text{H}^{14}\text{O}^{10}$  (Löwe).

On the preparation of tannic acid from nut-galls, see Rothe (*Arch. Pharm.* [2], cxlii. 232; *Jahresb.* 1870, 567).

**Reaction of Gallotannic Acid with Iodine and Alkali.**—When a drop of tannic acid solution is mixed with a cubic centimeter of  $\frac{1}{10}$  normal iodine-solution, the liquid on agitation immediately becomes colourless (with formation of gallic and ellagic acids); and if to this mixture there be added 1 c.c. of a spring water, which when boiled down to a small bulk exhibits only a faint alkaline reaction, a brilliant red coloration is produced, which lasts for a long time (Griessmayer, *Zeitschr. anal. Chem.* 1872, 43).

On the reaction of Tannic acid with Iodine and Starch, see Brauch (p. 1099).



**Estimation of Tannin.**—An elaborate memoir on the estimation of oak-bark tannin (quercitannin) has been published by C. Neubauer (*Zeitschr. anal. Chem.* 1871, 10; 1-40; *Chem. Soc. J.* [2], ix. 594-600; *Jahresb.* 1871, 964). Of the various methods in use, he gives the preference to that of Löwenthal, which is based on the use of a solution of potassium sulphindylate (indigo-carmine) standardised with permanganate. Wagner's method, founded on the precipitation of the tannin by cinchonine, Neubauer regards as unsound, inasmuch as even when the cinchonine solution is added in large excess, the filtrate still contains tannin.

A discussion of the different methods in use for the estimation of tannin in catechu, ratanhia, kino, and other tanning materials is given by Günther (*Russ. Zeitschr. Pharm.* ix. 161, 194, 225; *Vierteijahrschr. pr. Pharm.* xx. 214-238; *Chem. Centr.* 1871, 395).

On the use of tannin for the preservation of Wine, see *Dingl. pol. J.* cci. 376.

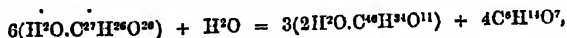
Contributions to the technology of the tannins: R. Wagner (*ibid.* ccv. 137-144).

Endeavours to establish the art of tanning on a scientific foundation: A. Reimer (*ibid.* ccv. 143, 248, 358, 457; *Jahresb. f. Chem.* 1872, 1016).

**Alder Tannin.** The coloured tannin of alder-wood has been examined by F. Dreykorn a. E. Reichardt (*Dingl. pol. J.* xciv. 157). The fresh sawdust of the wood of *Alnus glutinosa* was exhausted in an extraction-cylinder with boiling water; the dark red-brown filtrate precipitated with lead acetate; and the well-washed precipitate decomposed by hydrogen sulphide, the bulk of the colouring matter being thus thrown down together with the lead sulphide. The precipitate was washed with cold water, and the colouring matter extracted with boiling alcohol of 90 p.c. On distilling off the alcohol and drying the residue in the water-bath, there remained a brown resinous mass reducible by trituration to a red-brown powder.

The analysis of this body dried at 130° leads to the formula  $C^{27}H^{20}O^{11}$ . It is almost insoluble in ether, benzene, and carbon sulphide, dissolves with difficulty in absolute alcohol, more easily in boiling water, in all proportions of dilute alcohol. It precipitates gelatin, and produces a dirty green coloration with ferric chloride. By precipitating its hot aqueous solution with lead acetate, a lead compound is obtained having the composition,  $PbO.C^{27}H^{20}O^{10}$ ; the copper-compound contains  $3CuO.H^2O.4C^{27}H^{20}O^{10}$ .

**Alder Red.**—Alder tannin treated with dilute sulphuric acid (1 : 10) for 24 hours at the heat of the water-bath is resolved into sugar (18 to 19 p.c.; a fermentation experiment gave only 16 p.c.), and a red-brown resinous deposit of alder red, which when dried at 130° has the composition  $C^{16}H^{12}O^{13}$ , and when dried over sulphuric acid,  $C^{16}H^{12}(O^{13})^{13}H^2O$ . This substance is insoluble in water and in ether, slightly soluble in alcohol; caustic soda and ammonia dissolve it, forming a liquid of light red-brown colour, from which it is precipitated in flocks on acidulation; on exposure to the air, the alkaline solution becomes darker and deposits black-brown flocks. On adding lead acetate to a strongly ammoniacal solution of alder red, a brown precipitate is formed which, after drying at 130°, has the composition  $2PbO.C^{16}H^{12}O^{11}$ . The resolution of alder tannin into alder red and sugar may be represented by the equation:



which requires 22.1 p.c. of grape-sugar.

Alder tannin yields, by fusion with potash, protocatechuic acid, phloroglucin and acetic acid; and by dry distillation, pyrocatechin. As it is also split up by ferments, it is conceivable that the red colour which fresh alder-wood acquires by exposure to the air may be produced by alder red, the decomposition-product of alder tannin; at all events, the intensity of the colour agrees well with this supposition.

**TANTALATES and NIOBATES.** The following formulae for these minerals, deduced from numerous analyses, are given by Rammeisberg (*Berl. Acad. Ber.* 1871, 157, 406, 584; *Deut. Chem. Ges. Ber.* iv. 874; *Chem. Soc. J.* [2], ix. 196-204).

1. *Tantalite* and *Niobite* (columbite)  $\{nFeTa^3O^8\}$ , with isomorphous admixtures of the salts,  $FeSnO^3$ ,  $FeTiO^3$ ,  $FeWO^3$ .

2. *Tepiolite* is quadrate tantalite.

3. *Polycrase* and *Euxenite* differ from one another only as isomorphous mixtures. Crystallised polycrase contains 4 p.c. tantalic acid.

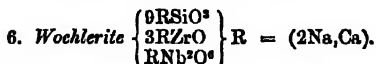
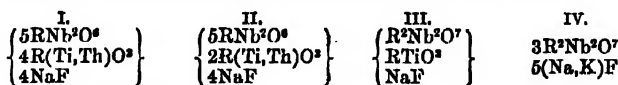


R = Y, Eb, Ce, U, Fe.

Water is present occasionally, but not as an essential constituent.

4. *Fergusonite*, *Yttrotantalite*, *Tyrite*, *Bragite*.—A combination of the same metals according to the formula  $R^2Nb^2O^6$ , or  $3R^2O.Nb^2O^3$ . Crystallised fergusonite from Greenland contains 1Ta : 12Nb. In these minerals also the water (sometimes amounting to 6 p.c.) is only a secondary constituent.

5. *Pyrochlore*.—Specimens from different localities show great diversity of composition, the only constant constituents being R=Ca and Ce, as also NaF. The analyses lead to the following formulæ: I. Miask; II. Brevig, containing uranium; III. Frederiksvärn, free from Th. and U., rich in Fe; IV. Kaiserstuhl.



For the analyses, see the paper above cited in the *Journal of the Chemical Society*; also the article TANTALUM in this dictionary, vol. v. pp. 667-669.

There are two tantalum and niobium minerals not included in these analyses, viz.: *samarskite* and *æschynite*. *Samarskite* is a niobate of uranium, yttrium, and iron (iv. 55); *æschynite*, a mixture of niobates, titanates, and thorates of Co, La, Ca, and Fe,

represented by the formula  $\left\{ \begin{array}{l} RNb^2O^6 \\ 2R(Ti,Th)O^3 \\ (Ti,Th)O^3 \end{array} \right\}$  (1st Suppl. 58).

A comparison of the composition of the natural tantalates and niobates, with their crystalline forms, exhibits several interesting series of isomorphous and heteromorphous bodies.

#### A. Isomorphous Groups of the Rhombic System.

	Ratio of the axes	
	a.	c.
Tantalite, Niobite	0.82	0.82
Wolfram	0.83	0.87
Tantalie acid	0.83	0.82
Tungstic acid	0.83	0.87
Titanic acid (Brookite)	0.84	0.94
Polycrase (Euxenite)	0.94	0.91
Æschynite	0.49	0.67
Wochlerite	0.99	0.75
Bronchite (MgSiO <sup>2</sup> )	1.03	1.18

#### B. Isomorphous Groups of the Quadratic System.

	Ratio of the axes	
	a.	c.
Tapiolite	0.62	0.64
Titanic acid (Rutile)	0.63	0.64
Zircon ((Zr.Si)O <sup>2</sup> )	0.63	0.64
Tin ore (SnO <sup>2</sup> )	0.63	0.67
Zirconic acid	1.00	1.00
Thoric acid	0.16	0.16
Xenotime (Y <sup>3</sup> P <sup>5</sup> O <sup>10</sup> )	0.62	0.62
Fergusonite	1.50	1.50
Scheelite (CaWO <sup>4</sup> )	1.53	1.53
Scheelbleierz (PbWO <sup>4</sup> )	1.57	1.57
Gelbbleierz	1.58	1.58

Hence it may be inferred:

1. The molecules  $RTa^2O^6$ ,  $RWO^4$ ,  $RTiO^3$  are isomorphous with the anhydrides  $Ta^2O^3$ ,  $WO^3$ ,  $TiO^2$ .

2. All these molecules are dimorphous. The regular form of pyrochlore is also connected with the forms of its component minerals.  $KF$  and  $NaF$ , like  $CaTiO^3$  (perovskite) are regular, and the same crystalline form is to be found in  $BaN^2O^6$ ,  $SrN^2O^6$ ,  $PbN^2O^6$ .

The tantalates and niobates hitherto found in minerals are  $RNb^2O^6$ ,  $R^2Nb^2O^7$ ,  $R^2Nb^2O^8$ , corresponding with the phosphates and arsenates.

**TANTALUM.** On the separation of this metal (and of niobium) from tin, titanium, and tungsten, see Rammelsberg (*Chem. Soc. J.* [2], x. 193, 194).

**TARTARIC ACID, C<sup>4</sup>H<sup>4</sup>O<sup>6</sup>.** *Formation from Oxalic Acid.*—This acid is formed, together with glycollic and glyoxylic acids, by the action of sodium-amalgam on ethylic oxalate in alcoholic solution:



(Debus, *Chem. Soc. J.* [2], x. 376); see also p. 569 of this volume.

On the Recovery of Tartaric and Oxalic acids from the residues of the Discharge process, see p. 881.

On the Heat of Neutralisation of Tartaric acid, see H<sub>2</sub>AT (p. 621).

**Reaction with Potassium Permanganate.**—This reaction takes place differently according as a mineral acid is added or not. To produce a permanent red coloration when no mineral acid is added, requires only half the quantity of permanganate solution that is necessary when an acid is added. In the former case a manganese tartrate,  $C^4H^4MnO^4 + 2H^2O$ , is formed, which is rose-coloured while moist, but becomes paler when dry, and is nearly colourless at  $100^\circ$  and higher temperatures. 1000 pts. of water dissolve 2.17 pts. of this salt. The boiling solution mixed with alcohol deposits small hard crystals. No acid salt is formed in the reaction (W. A. Fleischer, *Deut. Chem. Ges. Ber.* v. 350).

On the Detection of Tartaric acid crystals in Citric acid, see p. 346.

**Conversion of Dextrotartaric acid into Racemic acid and Inactive Tartaric acid.**—This transformation may be effected by heating the acid in sealed tubes. 30 grams of dextrotartaric acid are sealed up with 3 to 4 grams of water in strong tubes, and heated in an oil-bath to  $175^\circ$  for thirty hours. On opening the tubes a large quantity of gas escapes. The product is taken up by boiling water, and the solution is filtered and evaporated. If the concentration has not been carried too far, the crystals which separate consist entirely of racemic acid. The mother-liquor, which contains unaltered dextrotartaric acid, the inactive acid, and products of decomposition, yields, when again heated in sealed tubes, a further quantity of racemic acid. The temperature must be maintained exactly at  $175^\circ$ , since at higher temperatures the tartaric acid is decomposed, and at lower temperatures the transformation is very slow. The racemic acid thus obtained exhibits all the properties of that which is prepared from tartar. When the tartaric acid is heated without addition of water, the quantity of racemic acid obtained is smaller. For operations on a large scale, the materials may be heated in a wrought-iron autoclave. 650 grams of dextrotartaric acid and 100 grams of water thus heated to  $180^\circ$  yielded more than 100 grams of racemic acid. If the heat be continued long enough, the dextrotartaric acid disappears completely, while the quantities of racemic and inactive tartaric acid in the product bear to one another a certain fixed relation. To reconvert the inactive tartaric acid into racemic acid, it is necessary first to remove the racemic acid already formed. Consequently, pure inactive tartaric acid cannot be completely transformed into racemic acid by one treatment in the manner above described. Both the degree of heat and the quantity of water added have an influence on the state of equilibrium of the two acids in the mixture. Inactive tartaric acid may be obtained in considerable quantity by heating dextrotartaric acid with the above-mentioned quantity of water in the autoclave for two days to only  $165^\circ$ . After the small quantity of racemic acid formed at the same time has been removed by a first crystallisation, the mother-liquor is divided into two equal parts, one of which is neutralised with potassium carbonate, and then added to the other half. By this means the remainder of the racemic acid and the unaltered dextrotartaric acid may be removed in the form of thin, sparingly soluble, acid potassium salts. The mother-liquor of these salts yields the acid potassium salt of inactive tartaric acid, and on converting this into the calcium salt by precipitation, decomposing the latter with sulphuric acid, and filtering, the filtrate deposits free inactive tartaric acid in crystals (Jungfleisch, *Bull. Soc. Chim.* [2], xviii. 201).

**TARTRONIC ACID.** On the formation of this acid by the action of cupric oxide in alkaline solution on dextroglucose, see SUGARS (p. 1104).

**TARTROPHETHALIC ACID**,  $C^8H^{10}(OH)O^4$ . An acid formed by heating bromomalopthalic acid,  $C^8H^8Br(OH)O^4$ , with baryta-water. See TETRAHYDRO-PHTHALIC ACID (p. 1149).

**TAURINE.** *Behaviour in the Animal Organism.*—Schultzen considers the origin of urea and of sulphates in the urine to be due to the decomposition of bile-acids, first into cholic acid (excreted in the fæces), glycocine, and taurine, and finally into urea and sulphates, the sulphur in the taurine being thus viewed as oxidised in the body.

When men and dogs were fed on food impregnated with taurine, no increase of sulphates in the urine was noticeable, but almost all the taurine was excreted unchanged in the urine, no production of thiosulphates being discernible, even when 15 grams of taurine were given in three days; when, however, vegetable feeders, such as rabbits, were experimented on, only about  $\frac{1}{4}$  or less of the taurine was unattacked, about  $\frac{3}{4}$  being excreted as an alkaline thiosulphate, and more than  $\frac{1}{4}$  as a sulphate, this latter being probably due to a secondary action, whereby the thiosulphate became oxidised.

It hence appears that in vegetable feeders the sulphates in the urine are at any rate partially derived from taurine proceeding from the decomposition of bile; the whole of the urea, however, cannot be due to these changes, inasmuch as the relative quantities of nitrogen and sulphur daily excreted are very different from those which should

be present on Schultzen's supposition, the nitrogen being greatly in excess. Moreover, it is found that the normal urine of dogs fed on bread and milk contains only  $\frac{2}{3}$  of its sulphur as sulphates, the rest being in the form of sulphurized organic substances, so that the whole of the sulphur of the taurine formed is not oxidised to sulphate (E. Salkowski, *Deut. Chem. Ges. Ber.* v. 637).

**TAUROCHOLIC ACID.** On the estimation of this acid in bile, see Kütz (*Zeitschr. anal. Chem.* 1872, 353; *Jahresb. f. Chem.* 1872, 939; *Chem. Soc. J.* [2], xi. 536).

**TEA.** The difference in the quality of different samples of tea arises, not from their being the leaves of different species of tea-plant, but partly from the nature of the soil and manner of cultivation, and chiefly from the age of the leaves, the youngest leaves, other things being the same, yielding the best tea. The constituents of the ash of tea-leaves vary with their growth, the quantity of limo and silica increasing both absolutely and relatively with their age, whilst the potash and phosphoric acid decrease; and, as the best tea is prepared from the youngest leaves, an analysis of the ash would appear to be the simplest method of determining the quality of a tea. To test the truth of this inference, Ph. Zöller (*Ann. Ch. Pharm.* clviii. 180) examined a specimen of very fine and carefully made Himalaya tea, of a fine black colour, and consisting of very young lancet-shaped leaves. It contained 4.95 p.c. water, and 5.63 of ash, 100 pts. of which contained 39.22 of potash, 14.55 of phosphoric acid and only 4.24 of lime. As the tea consisted of very young leaves, and its ash was so rich in potash and phosphoric acid, it might be expected to yield a large amount of nitrogenous matter and of theine, and also of total extract. The nitrogen amounted to 5.38 p.c., and the extract, obtained by infusing 100 grams in three litres of boiling water twice successively, was 36.26 grams. To determine the theine, the tea was heated to 100° with slightly diluted sulphuric acid, treated with lead hydrate to remove the acid, and exhausted with 86 p.c. alcohol. The pale-coloured solution, on standing, deposited crystals which appeared to be theobromine, and the mother-liquor from these was found to contain 4.94 p.c. theine. No theobromine could be detected in two samples of the best tea of commerce used for comparison. Peligot's analysis (*ibid.* xlvii. 360) are the only published ones giving such high numbers for nitrogen and theine.

The extract gave 3.56 p.c. nitrogen, and 4.04 of ash, the latter containing 55.15 p.c. of its weight of potash, 7.89 phosphoric acid, and only 0.95 lime. The exhausted leaves gave 2.26 p.c. nitrogen and 1.80 of ash, containing only 7.34 of potash, but 25.41 phosphoric acid, and 10.79 of lime. It remains undetermined whether Himalaya tea is distinguished from Chinese tea by containing theobromine, but it would appear that the specimen examined was equal to the best Chinese tea.

The numbers above given show how easy it is, by an analysis of the ash, to detect a tea consisting of exhausted leaves which have been re-dried, since they become comparatively poor in potash salts and rich in lime. Zöller believes that the value of tea as a beverage is due, not only to the theine it contains, but also to the other nitrogenous substances present, and to the large amount of potassium salts.

Aubert (*Dingl. pol. J.* cxi. 500) finds that a cup of good Pekoe tea, prepared from 5 to 6 grams of the leaves, contains from 0.1 to 0.12 gram of theine, which is about the same amount as that contained in the infusion of half an ounce of good coffee.

**TELLURIUM.** *Preparation.*—According to F. Stolba (*Dingl. pol. J.* cxviii. 262), tellurium is completely precipitated from a solution of tellurous acid in excess of caustic potash or soda by boiling with grape-sugar; he recommends this method for the working of tellurium ores. Selenious acid is not reduced under the same circumstances.

*Spectra.*—On the spectrum of tellurium vapour, see Salet (*Compt. rend.* lxxiii. 559, 742); Ditte (*ibid.* 822); also *Chem. Soc. J.* [2], ix. 1145, 1146.

Tellurous chloride may be obtained by the action of dry chlorine on tellurium in a narrow tube, as a black mass which liquefies at a red heat, and volatilises in yellow vapours. A stratum of the vapour only a centimeter thick gives a peculiar spectrum, particularly well developed in the orange and green. Tellurous bromide gives a violet vapour, having its principal spectral lines in the red and yellow (Garnier, *Compt. rend.* lxxiv. 465).

On the Heat of Combustion of Tellurium, see Hnat (p. 613).

On the Reaction of Tellurium with Sulphuric anhydride, see SULPHUR (p. 1136).

*Hydrogen Telluride, TeH<sub>2</sub>,* is decomposed by heat in the same manner as hydrogen selenide (p. 1079). By enclosing tellurium in a tube filled with hydrogen, and heating only the part of the tube where the tellurium is placed, it is deposited on the cold part of the tube in prisms 20 mm. long (Ditte).

**TEREPHTHALIC ACID.** See PHTHALIC ACID (p. 979).

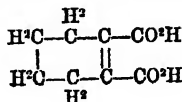
**TERPENES,  $C^{10}H^{16}$ .** On the physical character of terpenes, see OILS VOLATILE (p. 872); on their refractive indices, *LIGHT* (pp. 740, 741).

On the formation of Cymene from terpenes, see CYMENE (p. 419).

**TERTIARY ALCOHOLS.** *Oxidation.*—The oxidation of tertiary alcohols takes place according to a law similar to that which rules the oxidation of ketones (p. 711), the most simple alcohol-radicle remaining combined with the carbon-atom by which the whole group is kept together, whilst the two other radicles are oxidised separately. The only exception to this rule appeared to be made by trimethyl-carbinol, which, as Butlerow formerly found, yielded acetone, acetic acid, and propionic acid. But on studying the oxidation-products of this alcohol more closely, he now finds (*Zeitschr. f. Chem.* [2], vii. 484) that they consist chiefly of acetone (being an intermediate product) and acetic acid, besides a smaller quantity of isobutyric acid. The formation of this latter compound is not in contradiction to the above law; it is formed by a molecular change, corresponding with that by which Linnemann has found that derivatives of trimethyl-carbinol are obtained from isobutyl alcohol (p. 219).

**TETRAHYDROPHTHALIC ACID,  $C^8H^{10}O^4$**  (Baeyer, *Deut. Chem. Ges. Ber.* iii. 61; iv. 273). This acid is formed, with copious evolution of carbon dioxide, when hypopyromellitic acid (1st *Suppl.* 812) is heated. Tetrahydrophthalic anhydride,  $C^8H^8O^3$ , then distils over in the form of an oil, which solidifies in large laminae on cooling. This anhydride melts at  $68^\circ$  and distils in comparatively small quantities without alteration; it is insoluble in water, easily soluble in ether, and crystallises therefrom by spontaneous evaporation in hard shining laminae. It dissolves at a moderate heat in strong sulphuric acid, and is precipitated by water in large laminae. At a stronger heat gas is evolved, and the anhydride gradually undergoes complete decomposition without formation of phthalic or benzoic acid. The anhydride, when boiled with water, is converted into the easily soluble acid,  $C^8H^{10}O^4$ , which crystallises in laminae, melts at  $96^\circ$ , and is at the same time reconverted into the anhydride.

Tetrahydrophthalic acid is bibasic. When heated with distilled hydriodic acid it takes up 2 at. of hydrogen and is converted into hexhydrophthalic acid,  $C^8H^{12}O^4$ . The same compound is formed by the action of sodium-amalgam on tetrahydrophthalic acid, 2 at. of hydrogen appearing to be the largest amount that this acid is capable of taking up. This behaviour indicates that tetrahydrophthalic acid belongs to the series of benzocarbonic acids (1st *Suppl.* 809); Baeyer represents it by the constitutional formula:



This view of its structure is perfectly in accordance with its behaviour to bromine. When 2 at. bromine are added to its aqueous solution, a liquid is obtained which, when evaporated over sulphuric acid, yields hard crusts of bromomalophthalic acid,  $C^8H^{10}Br(OH)O^4$ . This acid dissolves freely in water, and is very easily decomposed. When heated with baryta-water it forms barium bromide and the barium salt of tartrophthalic acid,  $C^8H^{10}(OH)^2O^4$ . This last acid is very soluble in water, and crystallises therefrom in very large, finely developed prisms. When somewhat strongly heated it distils, leaving only a small residue. The syrupy distillate has a peculiar odour like that of the less hydrogenised aldehydes, and contains unaltered tartrophthalic acid, together with other substances. The acid is bibasic. Its barium salt separates in the cold in thin laminae, from warm solutions in granular prisms. The lead salt,  $C^8H^{10}O^4.Pb$ , crystallises in concentrically-united slender needles, very sparingly soluble in water.

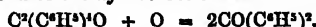
Hexhydrophthalic acid,  $C^8H^{12}O^4$ , is formed, as already stated, by the action of hydriodic acid or sodium-amalgam on tetrahydrophthalic acid; also, according to Mizoraki (*Deut. Chem. Ges. Ber.* iv. 558), by heating hydrophthalic acid,  $C^8H^8O^4$  (1st *Suppl.* 842), with hydriodic acid to  $240^\circ$ – $250^\circ$ . It melts at  $207^\circ$  (Mizoraki), at  $203^\circ$ – $205^\circ$  and solidifies in needles (Baeyer). It is a bibasic acid, and forms a crystalline lead salt,  $C^8H^{10}O^4.Pb + H^2O$  (Baeyer).

The formation of this acid from hydrophthalic acid is accompanied by that of another acid much more soluble in water, and melting at  $163^\circ$ – $167^\circ$ , also by that of a very small quantity of a hydrocarbon (Mizoraki).

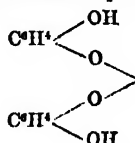
**TETRAMINES, CHROMIC.** See CHROMIUM (p. 336).

**TETRAPHENOL.** This name is given by Limpricht to a compound,  $C^4H^4O^2$ , produced by distilling barium pyromucate with soda-lime (p. 1032).

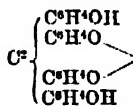
**TETRAPHENYLETHYLENE**,  $C^2(C^6H^5)^4$  (A. Behr, *Deut. Chem. Ges. Ber.* iii. 751; v. 277). This hydrocarbon is formed by the action of finely divided silver on the chloride,  $C^2(C^6H^5)^2Cl^2$ , obtained by treating benzophenone with phosphorus pentachloride (p. 176), and separates from solution in hot benzene in spicular crystals melting at  $221^\circ$ . On mixing its solution in glacial acetic acid with half its weight of chromic acid, likewise dissolved in glacial acetic acid, and boiling till the liquid turns green, the solution, on cooling, becomes filled with green needles of tetraphenylethylene oxide,  $C^2(C^6H^5)^2O$ , which, after several recrystallisations from glacial acetic acid, is obtained pure and melting at  $193^\circ$ – $194^\circ$ . The oxide dissolves in benzene and in ether, volatilises without residue when strongly heated, and is converted by chromic acid in excess—as also the hydrocarbon itself—into benzophenone:



Strong sulphuric acid converts tetraphenylethylene or its oxide into tetraphenylethylene-tetra-sulphonic acid, which, however, has not been obtained pure; its salts are easily soluble and uncrystallisable. On fusing the barium salt with three times its weight of potassium hydrate, tetraoxyphenyl-ethylene,  $C^2(C^6H^4OII)^2$ , is produced. This compound crystallises from acetic acid and melts above  $300^\circ$ . Ferric chloride dissolved in glacial acetic acid oxidises it to a crystalline body,  $C^2H^{12}O^4 \cdot \frac{1}{2}H^2O$ , which gives off its water at  $180^\circ$ . The crystals are green, with metallic lustre, and yield a red powder. They are insoluble in water, ether, chloroform, and benzene, slightly soluble in alcohol. Alkalis dissolve them with deep-blue green colour, and the concentrated solution yields, with acids, light or dark red precipitates. With alum the alkaline solution forms a dingy-red alumina-compound. The alkaline solution is easily reduced by zinc-dust. Behr regards this colouring matter as analogous in constitution to quinhydrone:



Quinhydrone

Colouring matter from  
Tetraoxyphenylethylene

**TETRAPHENYL-METHANE**,  $C(C^6H^5)^4$ , appears to be formed, together with benzophenone, by the dry distillation of barium benzoate, passing over chiefly in the higher boiling portions of the distillate (Behr, *Deut. Chem. Ges. Ber.* vi. 971).

**TETRASALICYLIDE.** See SALICYLIC ANHYDRIDES (p. 1067).

**TETROLIC ACID**,  $C^4H^4O^2$ . A solid acid, said by Geuther to be formed by the action of melting potash on the less volatile modification of monochlorocrotonic acid (p. 390).

**TETROXYETERIN.** A colouring matter obtained from the red spots over the eyes of the black-cock and pheasant; also from the reddish parts of the trout, the crab, and the fruit of *Phialepsis rubra*. It is soluble in chloroform, unchanged by caustic potash; concentrated sulphuric acid turns it indigo-blue, then black. It is also soluble in carbon sulphide and ether. It differs from the colouring matter of blood (Wurm, *Pogg. Ann.* cxlv. 170).

**THALLIUM**, Tl. *Atomic weight.*—Crookes has redetermined the atomic weight of this metal by ascertaining the quantity of thallous nitrate,  $TlNO^3$ , obtained by treating a known weight of thallium with nitric acid in a bulb-apparatus exhausted of air, with elaborate precautions to prevent access of atmospheric oxygen, and to eliminate any sources of error arising from inaccuracy in the weights employed, &c. The mean of ten closely agreeing determinations gave:

$$Tl = 203.642,$$

the minimum and maximum values being 203.628 and 203.666 (*Phil. Trans.* 1872; *Proc. Roy. Soc.* xx. 476).

*Occurrences.*—Thallium has been found in sphalerite from Geroldseck in the Breisgau (v. Kobell, *J. pr. Chem.* [2], iii. 176).

*Preparation.*—For the reduction of thallium from the chloride, Wöhler (*Ann. Ch. Pharm.* cxliv. 74) recommends the fusion of an intimate mixture of 20 pts. thallium chloride, 8 pts. sodium carbonate, and 1 pt. lampblack, at a low red heat. The slight

loss that may arise from volatilisation of the chloride at the commencement of the operation, may perhaps be avoided by making the mass into a paste with water, and drying it before fusion.

**Preservation.**—Böttger (*Dingl. pol. J.* cxvii. 379) recommends the keeping of thallium in distilled water freed from air. Thallium thus preserved was found to be quite unaltered after three years.

**Chlorides, Bromides, and Iodides** (Rammelsberg, *Pogg. Ann.* cxlvi. 592). *Thallium sesquichloride*,  $Tl^2Cl^3$  (or rather  $Tl^4Cl^6$ ), formed by melting thallious chloride in a stream of chlorine, is obtained in yellow scales. The same compound is formed when the brown oxide is dissolved in hydrochloric acid, and the solution evaporated.

*Potassio-thallic Chloride*,  $3KCl.TlCl^3 + 2H^2O$ , obtained by adding potassium chloride to a solution of the brown oxide in hydrochloric acid, forms large transparent crystals belonging to the quadratic or dimetric system. Almost similar crystals are obtained of the corresponding ammonium salt by using ammonium chloride in the place of potassium chloride. These salts are not decomposed by boiling with water, but are decomposed by alkalis, with separation of brown oxide of thallium.

*Potassio-thallic Bromide*,  $3KBr.2TlBr^3 + 3H^2O$ , is obtained by first precipitating the bromide of thallium, which is then dissolved by digestion with bromine-water, and, on the addition of potassium bromide, the double salt is formed. It is obtained in slightly yellow crystals, which appear to belong to the regular system.

*Potassio-thallic Iodide*,  $3KI.2TlI^3 + 3H^2O$ , is obtained by digesting thallious iodide with solution of potassium iodide and free iodine. By evaporation over sulphuric acid, the solution gives dark crystals which, when powdered, are of an intense dark red colour. The crystals belong to the regular system; on slight heating they lose iodine, and are converted into a mixture of potassium iodide and thallious iodide.

*Thaloso-thallic Iodide*,  $Tl^3I^4$  or  $5TlI.2TlI^3$ , is prepared by heating thallious iodide with strong hydriodic acid and iodine, and evaporating to dryness (at  $70^\circ$ ); by digesting thallious iodide with excess of iodine in ethereal solution; by dissolving thallious iodide in a solution of iodine in absolute alcohol, evaporating over sulphuric acid and washing the residue with absolute alcohol, or by precipitating a soluble thallic salt with potassio-thallious iodide. The last method, however, does not easily yield it pure (Jørgensen, *J. pr. Chem.* [2], vi. 82).

When a solution of thallious iodide in hydriodic acid mixed with iodine is slightly supersaturated with ammonia, and this solution is added by portions to a moderately dilute and gently warmed solution of *cuprammonium sulphate*, the double salt,  $4NH^3.CuI^2.2TlI^3$ , is precipitated in shining needles, which may be quickly washed with cold water and dried in the pressed state over calcium chloride. It is decomposed by prolonged washing, also by ammonia, in which it partly dissolves. Alcohol dissolves it with greenish-yellow colour. Heated to  $120^\circ$  it leaves a mixture of thallious and cuprous iodides, and when it is heated with zinc, all the iodine passes into solution, while thallium and copper remain behind in the metallic state together with the zinc.

**Oxygen-salts** (Rammelsberg, *loc. cit.*) *Thallic acetate* is easily obtained in rather large crystals by dissolving freshly precipitated thallic oxide in strong acetic acid. The crystals belong to the rhombic system, and, according to Wilm, have the composition  $Tl^4C^4H^4O^8$ , which is that of a basic salt.

*Thallious nitrate*,  $TlNO^3$ , is isomorphous with the rhombic nitrates of the monatomic metals, such as potassium, ammonium, and silver nitrates.

*Thallious perchlorate*,  $TlClO^4$ , belongs to the rhombic system, and is isomorphous with potassium perchlorate.

*Tri-thallic phosphate*, like the corresponding lithium salt, is almost insoluble. *Di-thallic phosphate* was obtained by Lang in the anhydrous state, but its crystalline form is unknown; the hydrate,  $2HTl^3PO^4 + aq.$  belongs, however, to the rhombic system. This latter salt agrees very closely in form with the salt  $Na^3HPO^4 + aq.$  *Mono-thallic phosphate*,  $H^3TlPO^4$ , and diammonium phosphate and arsenate, are isomorphous, and belong to the monoclinic system. From this it appears that in the three phosphates,  $R^3PO^4$ ,  $R^2HPO^4$ , and  $R^3HPO^4$ , H is isomorphous with R. The unequal hydration of the sodium salts disguises the isomorphism in this series. Thallium and potassium sulphates are also completely isomorphous, belonging to the rhombic system.

The double sulphates of thallium or potassium, with magnesium, zinc, nickel, or iron, are isomorphous; they belong to the monoclinic system. Thallium alum is also isomorphous with the ordinary alums.

Normal oxalate and bioxalate of thallium are crystalline, and belong to the monoclinic system; the quadroxalate is triclinic, and isomorphous with the corresponding potassium and ammonium salts.

Acid thallium tartrate is isomorphous with the potassium salt, and belongs to the rhombic system.

The double tartrates of thallium and sodium, and of thallium and antimony, are isomorphous with the potassium double salts. The picrates of thallium and of potassium and ammonium are, however, not isomorphous.

The ferrocyanides of thallium and rubidium are isomorphous, belonging to the triclinic system, and crystallising with 2 mols. of water.

On the Iodates and Periodates of thallium, see p. 683.

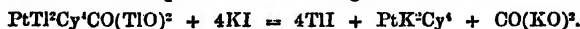
*Thallious uranate* is formed as a yellow precipitate resembling the uranates of the alkali metals, on adding thallious oxide to a solution of uranium (O. Bolton, *American Chemist*, 1872, ii. 456).

*Double Salt containing Thallium and Platinum*.—R. J. Friewell (*Chem. Soc. J.* [2], ix. 461) has obtained a salt having the composition  $\text{PtCl}^2\text{Cy}^4\text{CO}(\text{Tio})^2$ , by mixing hot solutions of potassio-platinous cyanide,  $\text{PtK}^2\text{Cy}^4 + 3\text{H}^2\text{O}$  (4.334 grams), and thallious carbonate (9.360 grams), whereupon the following reaction takes place:



It may also be formed directly by mixing 7.094 grams of potassio-platinous cyanide with 4.680 grams of thallious carbonate (and the corresponding barium salt by mixing 4.384 grams of bario-platinous cyanide with 9.360 grams of thallious carbonate).

The potassic double salt forms rectangular prisms, exhibiting a splendid crimson colour by transmitted light and by reflection, a deep bronze-green colour with strong metallic lustre. It is sparingly soluble in hot, insoluble in cold water. The aqueous solution is absolutely colourless, and does not deposit the salt on cooling, unless it is very concentrated; it yields, however, white crystals which are either a hydrate or a mixture of the two component salts simultaneously separated. It is best recrystallised from a solution of thallium carbonate too dilute to deposit that salt on cooling. The aqueous solution does not exhibit absorption-bands. The salt heated with nitric acid gives off carbon dioxide and leaves a red residue of thallium platinumocyanide. By potassium iodide it is decomposed in the following manner:



**THEBAICINE**. An alkaloid, probably isomeric with thebaine and thebenine (*infra*), produced from the latter under the influence of strong acids, especially of hydrochloric acid. From the resulting solutions it is thrown down by ammonia, as an amorphous yellow precipitate, insoluble in ether, benzoin, water, and ammonia, slightly soluble in hot alcohol, and separating again therefrom in the amorphous state. It dissolves in potash-ley, forming a solution which also absorbs oxygen. Strong nitric acid dissolves it with dark red, strong sulphuric acid with dark blue colour. Its salts are mostly resinous (Hesse).

**THEBAINE**,  $\text{C}^{10}\text{H}^{11}\text{NO}^3$  (Hesse, *Ann. Ch. Pharm.* cliii. 47; *Bull. Soc. Chim.* [2], xiv. 73; *Gmelin's Handbook*, xviii. 208). This base, discovered by Thiboumery (v. 758), is one of the constituents of the precipitate obtained by treating the aqueous extract of opium with excess of sodium carbonate or lime, exhausting the filtered liquid with ether, agitating the ethereal solution with acetic acid, and pouring the acid liquid into an excess of moderately dilute potash- or soda-ley, taking care that the precipitate does not agglutinate. By dissolving this precipitate in acetic acid, treating it with animal charcoal, combining it with tartaric acid, recrystallising the tartrate from a small quantity of boiling water, and separating it with ammonia, the thebaine is obtained perfectly pure. In this state it crystallises from hot dilute alcohol in beautiful, colourless, crystalline leaflets; from strong alcohol in prisms. It melts at  $193^\circ$  and may be sublimed. It is tasteless; its salts have an alkaline reaction. It dissolves easily in alcohol, benzene, and chloroform, sparingly in ether (1:140), and is nearly insoluble in water. From the solutions of its salts it is precipitated by potash, ammonia, lime and bicarbonate of sodium; ammonia and lime dissolve it to a certain extent.

Thebaine, though a strong base, is easily decomposable; a solution containing excess of hydrochloric acid decomposes in a few hours. Strong nitric and sulphuric acids decompose it, producing a deep red coloration; dilute sulphuric acid converts it into thebenine and thebaicene.

*Salts of Thebaine*.—The hydrochloride,  $\text{C}^{10}\text{H}^{11}\text{NO}^3\text{HCl} + \text{H}^2\text{O}$ , forms large rhombic prisms. The platinumchloride,  $2(\text{C}^{10}\text{H}^{11}\text{NO}^3\text{HCl})\text{PtCl}^4 + 4\text{H}^2\text{O}$ , is obtained as



an amorphous yellow precipitate, which soon changes to beautiful prisms; the water of crystallisation (only half, according to Andersen) is given off at  $100^{\circ}$ . The *hydriodide*, obtained by adding potassium iodide to the tartrate, forms colourless prisms easily soluble in water. The *neutral oxalate*,  $(C^{10}H^{11}NO^3 \cdot C^2H^2O^4 + 6H^2O)$ , forms white, cauliflower-like masses, soluble in 9.7 pts. of water at  $10^{\circ}$ , easily soluble also in alcohol, insoluble in ether. The *acid salt*,  $C^{10}H^{11}NO^3 \cdot C^2H^2O^4 + 11H^2O$ , forms large colourless prisms soluble in 44.5 pts. of water at  $20^{\circ}$ . The *acid tartrate*,  $C^{10}H^{11}NO^3 \cdot C^2H^2O^4 + H^2O$ , forms delicate prisms, easily soluble in hot alcohol and hot water, slightly soluble in cold water (1 : 130 at  $20^{\circ}$ ), having an acid reaction. The amorphous *neutral tartrate* is obtained by saturating the acid salt with thebaine, removing the excess of ether, and evaporating.

**THEBENINE**,  $C^{10}H^{11}NO^3$  (Hesse, *Ann. Ch. Pharm.* cliii. 47; *Bull. Soc. Chim.* [2], xiv. 73). This base, isomeric with thebaine, is obtained by heating the latter (10 pts.) to boiling with hydrochloric acid (200 pts. of sp. gr. 1.04), and immediately mixing the liquid with an equal volume of cold water. The crystals of the salt, which separate after several days, are recrystallised from hot water, and the base is separated by treating the solution with sodium thiosulphate.

Thebaine is amorphous, insoluble in ether and in benzine, slightly soluble in boiling alcohol, insoluble in ammonia, soluble in potash, precipitated therefrom by sal-ammoniac, neutralises hydrochloric and sulphuric acids. It absorbs oxygen rapidly, especially when in contact with basic substances. With acids it is more permanent; nevertheless, its hydrochloride, heated for a few minutes to  $100^{\circ}$  with hydrochloric acid, is converted into thebaïcine. Strong sulphuric acid dissolves thebaine with splendid blue colour, which disappears on addition of water, but is restored by further addition of sulphuric acid.

*Thebaine hydrochloride*,  $C^{10}H^{11}NO^3 \cdot HCl + 3H^2O$ , forms large crystalline laminae, easily soluble in boiling water and alcohol, sparingly in cold water (1 : 100), apparently not poisonous. The *platinochloride* is a brownish-yellow precipitate which quickly assumes a darker colour. The *mercurochloride*,  $2(C^{10}H^{11}NO^3 \cdot HCl) \cdot HgCl^2 + 2H^2O$ , crystallises in long colourless prisms mostly arranged in fan-shaped groups; effloresces in dry air. The *sulphate*,  $(C^{10}H^{11}NO^3)_2 \cdot SO^4H^2 + 2H^2O$ , separates on mixing the aqueous solution of the hydrochloride with sulphuric acid, as a white crystalline powder made up of prisms; it is nearly insoluble in cold and only slightly soluble in boiling water. The *acid oxalate*,  $C^{10}H^{11}NO^3 \cdot C^2H^2O^4 + H^2O$ , separates on adding oxalic acid to a hot solution of the hydrochloride, either as a crystalline precipitate or in satiny crystalline laminae, according to the degree of concentration. It is somewhat soluble in boiling water and crystallises therefrom in prisms.

**THEBOLACTIC ACID**. This supposed isomeride of lactic acid, obtained by T. and H. Smith from the mother-liquors of morphine (v. 759), has been examined by J. Y. Buchanan (*Deut. Chem. Ges. Ber.* iii. 182). By distilling 1 mol. of the calcium salt with 2 mols.  $PCl^5$ , treating the portion of the distillate boiling above  $111^{\circ}$  with alcohol, and that which boiled below  $111^{\circ}$  with water, he obtained from the first portion chloropropionic ether, and from the second chloropropionic acid, both of which were found to be identical with the bodies similarly prepared from ordinary lactic acid. Hence Buchanan regards it as in the highest degree probable that the so-called thebolactic acid is nothing but ordinary lactic acid. It is optically inactive, and its copper salt (contrary to the statement of T. and H. Smith) does not differ in any respect from that of ordinary lactic acid.

**THEBINE**. See CAFFEINE (p. 230).

**THELLITE**. A supposed silicate of yttrium, from S. Paolo, Brazil, called by this name, consists, according to Phipson (*Chem. News*, xxi. 13), of 90.00 p.c. silica, 4.56 ferric oxide, alumina and glucina, and 4.54 water, without a trace of yttria. It is perhaps an impure quartz.

**THERMO-REGULATORS**. An automatic thermo-regulator for use in the preparation of nitrous oxide and other gases, is described by F. Clowes (*Chem. Soc. J.* [2], ix. 639). Another thermo-regulator is described by E. Reichert (*Pogg. Ann.* cxliv. 467).

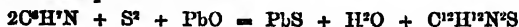
**THIOACETANILIDE**. See THIOANILINE.

**THIOALDEHYDE** or **SULPHALDEHYDE**,  $(C^2H^2S)^n$ . The molecular weight of this compound has been determined by Hofmann (*Deut. Chem. Ges. Ber.* iii. 588) in the same manner as that of the thioaldehyde of the methyl series (p. 1155) viz. by means of the vapour-density. Two determinations made in xyline-vapour gave for  $n$  the value 3, the numbers found being 89.4 and 90.0, while calculation for

$\frac{1}{2}(\text{C}^2\text{H}^4\text{S})^2$  gives 90. Hence it would appear that the so-called thioaldehyde is really thioparaldehyde, analogous to paraldehyde,  $(\text{C}^2\text{H}^4\text{O})^3$ .

**THIOAMYLIC ACID,  $\text{C}^2\text{H}^4\text{SO}_2$ .** An isomeride of amylsulphuric acid, said by Commaille (*Compt. rend.* lxxv. 1630; *Jahresb. f. Chem.* iii. 581) to be obtained, together with 'parathionic acid,' from the mother-liquors of corallin (p. 391). On concentrating the mother-liquor, and heating it several times, till water no longer throws down any colouring matter, then boiling it with litharge, pouring the hot liquid into cold water, and filtering, the filtrate yields on concentration, first crystals of parathionate, and then of thioamylate of lead. Thioamyllic acid is described as crystallising more readily than amylsulphuric acid, and its salts as more permanent, the barium salt as crystallising in needles containing 1 mol. water, whereas the amylsulphate contains  $2\text{H}_2\text{O}$  (v. 620). The ammonium, potassium and lead salts, as described by Commaille, differ more or less in crystalline form from the corresponding amylsulphates. As, however, the so-called parathionic acid has been shown to be not isomeric, but identical with ethylsulphuric acid (p. 897), it is not improbable that the slight differences between thioamyllic and amylsulphuric acids may be due to different degrees of purity.

**THIOANILINE,  $\text{C}^2\text{H}^3\text{N}^2\text{S} = (\text{C}^2\text{H}^3\text{NH})^2\text{S}$**  (Merz u. Weith, *Deut. Chem. Ges. Ber.* iv. 384). When 2 mols. aniline and 1 mol. sulphur are boiled together in a retort with reversed condenser as long as hydrogen sulphide continues to escape, a thick oil is obtained consisting of thioaniline and unaltered aniline, together with a large quantity of resin, probably containing more highly sulphuretted anilines. To purify the product, the aniline is distilled off with vapour of water, the residue is boiled with dilute hydrochloric acid, the solution evaporated to dryness, the residue dissolved in water; a small quantity of alkali added to precipitate impurities, and then a larger quantity, which throws down the thioaniline as a yellowish oil, which solidifies to a crystalline mass. It is further purified by solution in ether-alcohol, and precipitation as sulphate with sulphuric acid. Better results are, however, obtained when litharge is added to the boiling mixture of sulphur and aniline; the reaction then takes place as follows:



and only a small quantity of resin is formed. The product is exhausted with boiling alcohol, and the residue, which contains the thioaniline, treated as before.

Thioaniline is sparingly soluble in cold, more easily in hot water, very easily in alcohol and ether. From hot water it crystallises, with previous turbidity, in long thin satiny needles, which melt in boiling water, and at  $104^\circ\text{--}105^\circ$  when dry; it decomposes when distilled, yielding aniline, hydrogen sulphide, and a coaly residue.

The salts of thioaniline have an acid reaction; their solutions, even when very dilute, stain a deal shaving with a fine orange colour. Chlorine-water colours the solutions brownish-red, and then separates brownish flocks. Potassium dichromate forms a violet precipitate soluble in alcohol. Platinic chloride separates black flocks gradually at ordinary temperatures immediately on heating. Thioaniline heated with strong sulphuric acid forms a red to blue or blue-violet solution, which when poured into water produces a fine red colour.

Thioaniline hydrochloride,  $\text{C}^2\text{H}^3\text{N}^2\text{S} \cdot 2\text{HCl} + \text{H}_2\text{O}$ , forms long colourless needles or shorter prisms easily soluble in water, less in alcohol, nearly insoluble in ether. The sulphate,  $\text{C}^2\text{H}^3\text{N}^2\text{S} \cdot \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , crystallises from hot water in colourless shining prisms or spiculae, slightly soluble in cold water, nearly insoluble in ether and in alcohol. Ammonia added to the aqueous solution throws down, with partial decomposition, white nacreeous scales of a basic salt,  $(\text{C}^2\text{H}^3\text{N}^2\text{S})^2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ .

The resin obtained in the preparation of thioaniline from sulphur and aniline has, after boiling with dilute hydrochloric acid, treatment with warm concentrated hydrochloric acid, and precipitation with water, the composition  $\text{S}^2(\text{C}^2\text{H}^3\text{NH})^2 = 2\text{C}^2\text{H}^3\text{N}^2\text{S} + \text{S}$ .

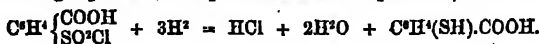
Thioacetanilide,  $(\text{C}^2\text{H}^3\text{NH} \cdot \text{C}^2\text{H}_3\text{O})^2\text{S}$ , is formed by the action of acetyl chloride or glacial acetic acid on thioaniline dissolved in benzene, as a crystalline mass easily soluble in hot, less easily in cold alcohol, slightly soluble in ether and in water, easily resolved by boiling dilute sulphuric acid into acetic acid and thioaniline sulphate. The product obtained with acetyl chloride melts at  $213.5^\circ$ , that prepared with acetic acid at  $215^\circ$ .

**Thiosulphocarbaniilides.**—When thioaniline is heated with carbon sulphide in alcoholic solution, hydrogen sulphide is evolved, and yellowish flocks are thrown down, which after washing with alcohol and ether, and boiling with carbon sulphide, consist of a mixture of two sulphocarbaniilides, viz.:



The mixture is microcrystalline, and melts with decomposition at a high temperature. Boiling concentrated sulphuric acid acts rather slowly on it, producing hydrogen sulphide, carbon dioxide, and thioaniline, but apparently no product analogous to mustard oil.

**THIOBENZOIC ACID**,  $C^6H^4O^2S = C^6H^4(SH).COOH$ . *Thiohydrobenzoic acid* (Hübner a. Upmann, *Zeitschr. f. Chem.* iii. 291).—This acid is produced by the action of nascent hydrogen (from tin and hydrochloric acid) on sulphobenzoic chloride (obtained by heating 1 pt. sodium sulphobenzoate with 2 pts.  $PCl^3$ ):



The crystalline mass which separates is washed with hydrochloric acid, dissolved in ammonia, precipitated by hydrochloric acid, and recrystallised from hot alcohol.

Thiobenzoic acid is nearly insoluble in water, slightly soluble in alcohol, and crystallises from the latter in faintly yellowish needles, melting at  $242^{\circ}$ – $244^{\circ}$ .

*Ammonium thiobenzoate*,  $C^6H^4(SH)CO^+NH^4 + H^2O$ , is a granulo-crystalline mass soluble in water and alcohol. The *barium salt*,  $[C^6H^4(SH)CO^+]^2Ba + 2\frac{1}{2}H^2O$ , is obtained by precipitating a boiling, very dilute solution of the ammonium salt with barium chloride, in small, white, prismatic needles. The *calcium salt*,  $[C^6H^4(SH)CO^+]^2Ca + 3H^2O$ , and the *lead* and *zinc* salts, are likewise obtained by precipitation.

When thiobenzoic acid is shaken up with 1 mol. bromine, hydrobromic acid is given off, and an acid is formed, probably dithiobenzoic acid,  $(C^6H^4)^2S(CO^2H)^2$ .

*Metabromothiobenzoic acid*,  $C^6H^4Br(SH)COOH$ , is obtained, similarly to the preceding, from bromosulphobenzoic acid. The crystalline mass separated by the action of tin and hydrochloric acid on bromosulphobenzoic chloride, dissolves for the most part in alcohol, and the solution when left to evaporate deposits the acid in small colourless needles melting at  $264^{\circ}$ – $266^{\circ}$ , insoluble in water, easily soluble in alcohol.

**THIOFORMALDEHYDE**,  $(CH^2S)^2$ . *Methylene Sulphide*.—This body, first obtained by Girard by the action of nascent hydrogen on carbon sulphide (iii. 1007), is also produced by the action of sodium sulphide on methylene iodide (Huseman, *loc. cit.*), and by that of hydrogen sulphide on formaldehyde (Hofmann, 1st *Suppl.* 622). Its alcoholic solution mixed with silver nitrate yields a precipitate which, when washed with alcohol and dissolved in hot water, crystallises on cooling in thick rhombic laminae having the composition  $(CH^2S)^2.AgNO^3 + H^2O$ , and giving off their water at  $100^{\circ}$ . A solution of this salt in excess of silver nitrate yields  $(CH^2S)^2.2AgNO^3 + \frac{1}{2}H^2O$ , which also becomes anhydrous at  $100^{\circ}$  (Hofmann, *Deut. Chem. Ges. Ber.* ii. 152; iii. 584; Girard, *Compt. rend.* lxx. 625). The solution of the thioaldehyde boiled with platonic chloride yields a crystalline precipitate having, according to Hofmann, the composition  $2C^6H^4S^2.PtCl^4$ ; according to Girard  $2C^6H^4S^2.PtCl^3 + 2(C^6H^4S^2.PtCl^4)$ .

Hofmann also finds that the precipitate sometimes contains platinous chloride, arising from partial reduction of the platonic chloride, but not in constant proportion. By mixing a solution of platinous chloride in hydrochloric acid with an alcoholic solution of thioformaldehyde, he obtained a light yellow precipitate having the composition  $3C^6H^4S^2.2PtCl^3$ .

From the preceding results, Hofmann infers that the molecular formula of thioformaldehyde is  $C^6H^4S^2$ , and this conclusion is confirmed by the vapour-density. Two determinations (in xylidine vapour) gave the values 72.0 and 73.2, the calculated value for  $\frac{1}{2}C^6H^4S^2$  being 69.

According to Girard, thioformaldehyde, heated to  $170^{\circ}$  in a closed vessel with sulphate or borate of silver, is converted into dioxymethylene,  $(CH^2)^2O^2$  (iii. 1006).

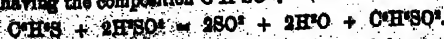
**THIOHYDROBENZOIC ACID**. Syn. with THIOBENZOIC ACID.

**THIOISOPROPYL ALCOHOL**,  $CH(CH^3)^2SH$ . Syn. with ISOPROPYL SULPHIDE (p. 1006).

**THIOYL CHLORIDE**,  $SOCl$ . See SULPHUR CHLORIDES.

**THIOFARALDEHYDE**. See THIOALDEHYDE (p. 1153).

**THIOPHENOL**,  $C^6H^4SH$ . *Phenyl Sulphhydrate*, *Phenyl Mercaptan*.—This compound dissolves in cold sulphuric acid, with evolution of sulphur dioxide, forming a fine blue solution, which, on dilution with water, becomes colourless and deposits a reddish body having the composition  $C^6H^4SO^3$ :



The substance thus formed as an isomeric of benzene-sulphurous acid or phenyl-

sulphurous hydride (v. 564; 1st Suppl. 275), from which, however, it differs greatly in its properties (Brunner, *Deut. Chem. Ges. Ber.* iv. 984).

On the formation of Phenyl Bisulphite from thiophenol, see PHENYL SULPHIDES (pp. 941, 942).

**THIORESORCIN**,  $C^6H^4S^2$ . This compound is formed by the action of tin and hydrochloric acid on benzene-disulphonic chloride,  $C^6H^4(SO^2Cl)^2$  (produced by treating the sodium salt of benzone-disulphonic acid [1st Suppl. 275] with phosphorus pentachloride). Thioresorcin melts at  $27^\circ$  and boils at  $243^\circ$ . Its alcoholic solution forms with lead acetate an orange-coloured precipitate, with copper salts a green, and with silver salts a light yellow precipitate (O. Pазебке, *J. pr. Chem.* [2], ii. 418).

**THIOSULPHOCARBANILIDE**. See THIOANILINE (p. 1164).

**THIOUREA**. A sulphuretted compound obtained as a secondary product in the preparation of leucinitril by Thudichum's method (p. 736).

**THIOTOLUIDINE**,  $C^6H^4N^2S$  =  $(C^6H^4NH^2)^2S$  (Menz a. Weith, *Deut. Chem. Ges. Ber.* iv. 384). This base is prepared, like thioaniline, by heating toluidine and sulphur together, with addition of litharge. It crystallises from alcohol in large colourless laminae resembling naphthalene, dissolves easily in ether and in alcohol, sparingly in water, whether cold or hot, melts at  $103^\circ$  to  $103.5^\circ$ . It unites easily with acids, forming well-crystallised salts which are decomposed by a large quantity of water, still retaining a strong acid reaction. The hydrochloride,  $C^6H^4N^2S.2HCl$ , crystallises in long, colourless, highly lustrous, anhydrous prisms. Platonic chloride throws down from its concentrated solutions slender yellow needles of the salt,  $C^6H^4N^2S.2HCl.PtCl_4$ . The sulphate,  $C^6H^4N^2S.H^2SO_4$ , is thrown down by sulphuric acid from alcoholic solutions of the base, as a dazzling, white, anhydrous precipitate. It is decomposed by boiling water, with separation of the base, but crystallises from water acidulated with sulphuric acid, in wavelitic groups of needles containing 2 mols. water of crystallisation.

Hot concentrated sulphuric acid dissolves thiotoluidine, forming a solution which is nearly colourless at first, but afterwards becomes malaga-brown. Acid solutions of the base heated with oxidising agents (as ferric chloride, potassium dichromate, potassium chlorate, and hydrochloric acid, &c.) are coloured first yellow, then brown-red, then raspberry-red, and finally deposit dark coloured flocks. Chlorine-water, even in the cold, colours them deep yellow-red.

**THYMOQUINONE**,  $C^6H^4(O^2)^2$ . See THYMOL, under PHENOLS (p. 935). Lallemand's *thymid*,  $(C^6H^4O^2)$ , produced by mixing the alcoholic solutions of thymoquinone (thymoil) and thymohydroquinone (thymoilol), is in reality thymoquinhydrone,  $C^6H^4O^2 = C^6H^4O^2$  (thymoquinone) +  $C^6H^4(OH)^2$  (thymohydroquinone). See further, *Chem. Soc. J.* [2], ix. 350-354.

**Bromothymoquinones** (Carstanjen, *J. pr. Chem.* [2], iii. 50). When thymoquinone is heated with two molecules of bromine under water till the smell of bromine is no longer perceptible, a clear dark red oil is formed, which, after repeated washing with cold water, speedily solidifies to a hard yellowish-red crystalline mass, consisting of a mixture of mono- and di-brominated thymochinone.

**Dibromothymoquinone**,  $C^6H^4Br^2(O^2)^2$ .—The crystalline mass dissolves with tolerable facility in boiling alcohol, the solution depositing, as it cools, an abundance of fine, lustrous, pale yellow laminae, which are obtained perfectly pure by washing with cold alcohol. In the dry state this substance forms extremely light, shining, pale yellow laminae resembling chloranil. It melts to a pale yellow liquid at  $73.5^\circ$ . On exposure to light it gradually assumes a reddish colour. When it is treated with tin and hydrochloric acid, the group  $(O^2)^2$  is converted into  $(OH)^2$ , the bromine being at the same time displaced by hydrogen, so that normal hydrothymoquinone is produced.

**Monobromothymoquinone**,  $C^6H^4Br(O^2)^2$ , is contained in the mother-liquor of dibromothymoquinone, and crystallises in long yellow needles on spontaneous evaporation of the solution; it has not, however, been obtained quite free from the dibromo-compound. The impure product dissolves with brownish-red colour in warm aqueous potash-ley; dilute acids throw down from the solution a yellow flocculent powder, which, after drying, sublimates in splendid scarlet crystals. This body is oxythymoquinone,  $C^6H^4(HO)(O^2)^2$ , the formation of which confirms the existence of monobromothymoquinone.

**Oxythymoquinone**,  $C^6H^4(HO)(O^2)^2$  (Carstanjen, *loc. cit.*), is also obtained by distilling diamidothymol hydrochloride,  $C^6H^4(HO)(NH^2)(HCl)$ , with ferric chloride in a current of steam. The reaction in this case evidently resembles that observed by Gribe and Ludwig in the case of diamidonaphthal (p. 831).

Oxythymoquinone crystallises from hot alcohol, in which it is easily soluble, in perfectly regular rhombic tables, the angles of which approximate to those of the cube, and from ether in irregular crystals having curved faces. It melts at  $187^{\circ}$  (uncorr.) in a capillary tube, and sublimes without decomposition in splendid glittering scarlet crystals.

As might be expected from the accumulation of electronegative groups, the hydrogen of the hydroxyl is not displaceable by acetyl, the substance being unacted upon by acetyl chloride. On the other hand, this hydrogen is readily displaced by basic radicals. Oxythymoquinone is converted by ethyl iodide at  $100^{\circ}$  into *ethoxythymoquinone*,  $C^{10}H^{11}(C^2H^5O)(O^2)^2$ , which sublimes completely in golden-yellow laminae. Aniline in alcoholic solution also acts immediately on a solution of oxythymoquinone; the liquid assumes a dark purplish-brown colour, and after evaporation the residue yields, by sublimation, beautiful violet needles having a brilliant metallic lustre, melting to a purple liquid above  $200^{\circ}$  and dissolving very freely in alcohol.

Oxythymoquinone is not easily acted on by reducing agents. On warming it with tin and hydrochloric acid, oxythymohydroquinone,  $C^{10}H^{11}(OH)^2$ , is produced. This body is a white crystalline mass, easily soluble in water, forming a solution which instantly turns yellow and deposits oxythymoquinone on exposure to air.

*Dioxythymoquinone*,  $C^{10}H^{11}(HO)^2(O^2)^2$ , is formed when dibromothymoquinone, moistened with alcohol, is dissolved in warm potash-ley, and the dark-brown solution is decomposed by dilute acids. The brownish-yellow flocks thereby thrown down, after being washed with hot water, dissolve in warm alcohol, which deposits crystals on evaporation, always contaminated, however, with a brown resinous substance, difficult to separate. The pure substance has not yet been analysed (Carstanjen).

**TIGLIO ACID**,  $C^8H^8O^2$ . An acid obtained from croton oil (p. 395).

**TIN.** *Disaggregation by Cold.*—Blocks of Banca tin, exposed to the air at St. Petersburg in the cold winter of 1867–68, swelled up, and acquired a fibro-crystalline structure, and were partly broken up into fragments of the same structure, partly crumbled to a granulo-crystalline powder. The cavities in the interior were lined with a metallically lustrous film, while the crystalline fragments themselves appeared dull (Fritzsche, *Pogg. Ann.* cxxvi. 176). A similar disintegration was observed in nearly pure block tin, containing only 0.3 p.c. foreign metals (lead and iron), which was sent from Rotterdam to St. Petersburg by rail during very cold weather in 1871 (Oudemans, *Instist.* 1872, 142).

According to F. Lewald (*Dingl. pol. J.* cxvii. 369) it is only block tin that disintegrates at low temperatures, the effect being due to the strong tension of the external parts produced by the previous casting and sudden cooling, this tension increasing as the temperature falls, and finally leading to disruption.

On a peculiar state of the molecules of tin, see further, Fritzsche (*Ann. Chim. Phys.* [4], xxvi. 321).

*Specific Gravity.*—Rammelsberg (*Deut. Chem. Ges. Ber.* iii. 724) found the specific gravity of the disintegrated tin described by Fritzsche to be 7.195; after fusion it rose to 7.310. The specific gravity of previously fused tin is, according to the accordant experiments of several observers, = 7.2905–7.299, whereas W. H. Miller (*Berg. Jahresh.* xxiv. 138) found, for tin deposited by electrolysis in quadratic crystals, a specific gravity = 7.178, which, however, rose after fusion to 7.293. Rammelsberg also found the specific gravity of tin reduced from stannous chloride by a feeble current to be 7.143 to 7.166, whence he infers that tin is dimorphous. After fusion it has a still undetermined, perhaps regular form, and in this form a specific gravity of 7.29; but by exposure to cold this form passes into a quadratic form, which the tin likewise assumes when reduced in the wet way, and in this form it has a specific gravity of 7.14–7.18. The decrease of volume of the last-mentioned form by heat is hereby explained.

The *specific heat* of tin, as determined by the ice-calorimeter (p. 595), is for cast-tin 0.559, for allotropic tin 0.546 (Bunsen).

*Spectra.*—The haloid compounds of tin impart to a hydrogen-flame a blue colour which may be ascribed to stannic oxide. The nucleus of this flame consists, however, of two concentric cylinders. The inner, which is nearly cold, is blue with chloride, green with bromide, yellow with iodide of tin, and always gives a continuous spectrum. It is surrounded by a somewhat warmer carmine-red sheath, the spectrum of which is reduced to a narrow bright line and an indistinct band, the former being near the second lithium line.\* Bromide of tin in a cooled flame produces an emerald-green colour, with continuous spectrum (Salet, *Compt. rend.* lxxiii. 862; *Chem. Soc. J.* [2], ix. 1147).

\* This is the colour first observed by Barrett (*Phil. Mag.* [4], xxx. 321).

**Action of Nitric Acid.**—G. Hay (*Chem. News*, xxii, 298) observes that pieces of tin about the size of pins' heads dissolve slowly at 2-2° in pure nitric acid diluted with an equal volume of water, forming a perfectly clear yellow solution which becomes colourless when gently heated and deposits metastannic hydrate on boiling. W. L. Scott (*ibid.* 322) states that he observed this fact some time ago, and adds that the separation of metastannic acid takes place at temperatures above 5°, or even lower, if the solution be exposed to a bright light.

**Separation of Tin from other Metals.**—To separate tin from arsenic and antimony, F. W. Clarke (*Zeitschr. anal. Chem.* ix, 487) boils the mixed solution with excess of oxalic acid, and passes hydrogen sulphide into the liquid to saturation. The arsenic and antimony are said to be thereby completely precipitated, while the tin remains in solution. To separate tin from molybdenum, the solution is mixed with excess of alkaline sulphide, the resulting sulphur salts decomposed with hydrochloric acid, and the precipitated sulphides of tin and molybdenum boiled with aqueous oxalic acid, which dissolves only the tin. If the tin was originally present as stannous salt, the resulting stannous oxalate must be dissolved in dilute hydrochloric acid.

To estimate the tin in the oxalic acid solution, ammonium is added in excess, then ammonium sulphide in sufficient quantity to redissolve the precipitate first produced, and finally the liquid is supersaturated with acetic acid, and left in a warm place. The resulting precipitate of stannic sulphide and oxide is washed with ammonium nitrate, ignited and weighed. According to G. C. Wittstein (*Zeitschr. anal. Chem.* ix, 490), the mode of separation just described is worthless, at least as applied to the separation of tin from arsenic and antimony, the precipitation of these two metals being very incomplete, and a considerable portion of the tin being precipitated with them.

For the separation of tin from antimony, see also p. 97.

The separation of tin from tungsten may be easily and completely effected by fusing a mixture of stannic and tungstic oxides with potassium cyanide in a porcelain crucible till the stannic oxide is reduced. The fused mass is lixiviated with water, the liquid filtered to separate the tin from the potassium tungstate, and the tin is washed with hot water, oxidised with nitric acid, and weighed as stannic oxide. The tungstic acid is best determined directly, after the potassium cyanide has been decomposed (J. H. Talbutt, *Deut. Chem. Ges. Ber.* iv, 279).

**Chlorides.** When chlorine not perfectly dry is passed over heated metallic tin, there is formed, in addition to anhydrous stannic chloride, a small quantity of a white crystalline sublimate having the composition  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ . If a very small quantity of water be added to this compound, or it be allowed to deliquesce, sulphuretted hydrogen precipitates the ordinary yellow stannic sulphide; but if it be dissolved in a large quantity of water, a yellowish-brown precipitate is produced by the same reagent. This may be attributed to the formation, by the excess of water, of metastannic chloride, from the solution of which the yellowish-brown metastannic sulphide is precipitated by sulphuretted hydrogen. Metastannic chloride is also produced when water is added to ordinary stannic chloride. This change is prevented by free acid, especially if water be not present in great excess. On dissolving several quantities of the same sample of tin in *nitro-muriatic acid*, and subsequently decomposing with sulphuretted hydrogen, stannic sulphide differing in colour was produced, probably in consequence of the formation of variable quantities of metastannic sulphide (H. Scheerer, *J. pr. Chem.* [2], iii, 47).

**Chlorobromides.**—When bromine is added by drops to stannous chloride, the violence of the reaction being moderated by cooling, it is found that to convert the whole of the stannous chloride into a stannic compound, 1 mol. bromine ( $\text{Br}_2$ ) must be added for each molecule of  $\text{SnCl}_2$ . The product is a yellow, strongly fuming liquid, having a very high specific gravity and easily decomposed by water. When distilled it begins to boil at 130°, the temperature slowly rising to 190°, at which the last drops pass over. Products of constant boiling point have not been obtained, but analysis showed that the higher-boiling portions were comparatively rich in bromine, the lower in chlorine, the reaction perhaps taking place as shown by the equation:



(Ladenburg, *Ann. Ch. Pharm., Suppl.* viii, 60).

**Stannic Oxide and Acids.** *Stannone* from the San Jacinto mine in San Bernardino, California, where it occurs in small grains and more rarely in larger crystals with topaz and quartz, has been analysed by F. A. Genth (*Chem. News*, xii, 334) with the following results:

$\text{SnO}_2$	$\text{WO}_2$	$\text{SiO}_2$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$
88.00	1.08	7.20	0.32	0.40
79.15	0.22	9.52	0.27	13.84

Consisting of Fe, Mn,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ , CaO,  $\text{Fe}_2\text{O}_3$ , &c.

Twin crystals of tinstone from the granite veins of S. Piero, in Eiba, are described by G. vom Rath (*Jahrb. f. Min.* 1870, 890), who further remarks that only one other occurrence of tinstone in sporadic crystals of this kind is known, viz. at Chesterfield in Massachusetts.

A block of so-called 'Jew's tin,' or 'Jews'-house tin,' from Tremethack Moor in Cornwall, was found to be partially covered with a hard, brittle, brown crust, containing 90 p.c. stannic oxide, with small quantities of metallic tin, stannic chloride, ferric oxide, and silica. This crust somewhat resembles the native variety of stannic oxide called 'wood-tin,' and has probably been formed by the slow oxidation of the outer surface of the block (J. H. Collins, *Chem. News*, xxv. 271).

On the supposed crystallisation of stannic oxide from fused microcosmic salt, see PHOSPHATES (p. 976).

On the reaction of stannic oxide with phosphorous chloride, see p. 976.

**Metastannic Acid.**—According to A. H. Allen (*Chem. Soc. J.* [2], x. 274), the properties of this acid are somewhat different from those ordinarily assigned to it (v. 820). When the metastannic acid prepared by treating tin with nitric acid, and washing, is boiled for some minutes with a moderate quantity of strong hydrochloric acid (sp. gr. 1.11), a certain quantity of tin is dissolved, and, on adding a larger quantity of hydrochloric acid, almost complete dissolution takes place. The residue exhibits the properties commonly assigned to metastannic acid, excepting that its aqueous solution is less inclined to be precipitated by an excess of hydrochloric acid. The liquid poured into cold water gave at first a precipitate of stannic sulphate, but soon afterwards a precipitate of orthostannic acid. Commercial stannic acid (free from lead) dissolves only partially in strong sulphuric acid.

**Stannates.**—P. H. Vaughan (*Deut. Chem. Ges. Ber.* v. 396) prepares the stannates of the alkali-metals on the large scale by treating tin-clippings with caustic potash (or soda-loy) of sp. gr. 1.2, decanting the liquid, pumping air (or oxygen) through the vessels containing the metal, pouring the decanted solution again upon the metal, and repeating this treatment till the greater part of the alkaline liquid has been converted into a tin-solution. The reaction may be accelerated by gently warming the liquid and heating the air which is passed over the metal.

**Compound of Stannic oxide with Acetic oxide.**—When 2 pts. of acetic oxide and 1 pt. of metastannic acid, dried at 100°, are heated together for two or three hours to 150° in sealed tubes, a syrupy liquid is obtained, which solidifies, on cooling, to long needles having, when pressed and dried in a vacuum over quicklime, the composition  $\text{SnO}_2 \left[ \begin{smallmatrix} \text{C}^2\text{H}^3\text{O} \\ \text{C}^2\text{H}^3\text{O} \end{smallmatrix} \right] \text{O}$ . After washing with pure ether and drying in a vacuum, the

crystals exhibit the composition  $\text{SnO}_2 \left\{ \begin{smallmatrix} \text{C}^2\text{H}^3\text{O} \\ \text{C}^2\text{H}^3\text{O} \end{smallmatrix} \right\} \text{O}$ . When exposed to the air, they are converted into an amorphous glassy mass having the composition  $\text{SnO}_2 \cdot \text{C}^2\text{H}^3\text{O} \cdot \text{OH}$  (Laurence, *Compt. rend.* lxxiv. 1524).

**TIN-RADICLES, ORGANIC.** 1. **Stannethyls** (Ladenburg, *Ann. Ch. Pharm., Suppl.* viii. 60; *Deut. Chem. Ges. Ber.* iii. 353, 647). **Stannotriethyl iodide**,  $\text{Sn}(\text{C}^2\text{H}^5)_3\text{I}$ , is prepared by acting on 100 grams of sodium stannate containing 14 p.c. of tin with 80 grams of ethyl iodide in a flask provided with a reversed condenser, gentle heat being at first applied to set up the action, and the flask afterwards cooled to prevent it from becoming too violent. The mixture is afterwards heated in the water-bath, and finally to 150° in an oil-bath, and after the flask has cooled the contents are distilled in a sand-bath. In this way a product is obtained consisting of stannotriethyl iodide and stannotetethyl, which latter may be converted into stannotriethyl iodide by the action of hydriodic acid, just as the corresponding chloride is obtained by the action of hydrochloric acid (v. 832). This iodide,  $\text{Sn}(\text{C}^2\text{H}^5)_3\text{I}$ , boiling at 231°, is converted into **stannotriethyl** by the action of sodium, the flask containing it being connected with a reversed condenser by means of a Y-tube, through which the sodium is dropped. It is ultimately heated to 200°, and, after cooling, the stannotriethyl is separated from the sodium iodide by dry ether. On distilling off the ether, crude stannotriethyl remains as a liquid, boiling with partial decomposition at 265°–270°. It decomposes, with separation of tin, even when distilled in a current of carbon dioxide or hydrogen, but, by distilling it under a low pressure, it may be obtained pure.

Stannotriethyl is a liquid of sp. gr. 1.4115 at 0°, and having the pungent odour of the stannotriethyl-compounds; it is insoluble in water and in aqueous alcohol, and precipitates silver from an alcoholic solution of the nitrate. Two vapour-density determinations gave the numbers 14.70 and 14.93 ( $H=1$ ), showing that the molecular formulae of the compound is not  $\text{Sn}(\text{C}^2\text{H}^5)_3$ , but  $\text{Sn}^2(\text{C}^2\text{H}^5)_4$  (analogous to ethane) which remains to be proved.

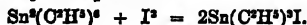


*Stannodiethyl chloride*,  $\text{Sn}(\text{C}^2\text{H}^5)_2\text{Cl}_2$ , is obtained by passing chlorine into a solution of stannotriethyl in chloroform, or better in carbon tetrachloride, and remains, after evaporation of the solvent, in beautiful silky crystals which, after drying over sulphuric acid, melt at  $85^\circ$  (at  $60^\circ$  according to Cahours, v. 827). The *iodide*,  $\text{Sn}(\text{C}^2\text{H}^5)_2\text{I}_2$ , formed from it by precipitating with ammonia and dissolving the precipitate in hydriodic acid, melts, according to Ladenburg, at  $44.5^\circ$  (at  $42^\circ$  according to Frankland, v. 827).

The formation of stannodiethyl chloride from stannotriethyl and chlorine is represented by the equation:



To ascertain what might be the first mode of action of the halogen, Ladenburg added 1 mol. iodine to 1 mol.  $\text{Sn}^2(\text{C}^2\text{H}^5)_3$ , avoiding rise of temperature, and found that the action took place as shown by the equation:



The production of the compound,  $\text{Sn}(\text{C}^2\text{H}^5)_2\text{I}_2$ , by decomposition of stannotriethyl with iodine (Cahours, v. 829), is regarded by Ladenburg as doubtful. Stannotriethyl, treated with halogens, produces in fact only bodies of the type  $\text{SnX}_4$ , the union between the two tin-atoms being first dissolved, and then the ethyl group replaced by halogens, a mode of action by which tin is essentially distinguished from carbon and silicon. Stannotriethyl, heated with strong hydrochloric acid, gives off inflammable gases, and an oil which solidifies, on cooling, to a mass which melts at  $83^\circ$ , and appears to be a mixture of  $\text{Sn}(\text{C}^2\text{H}^5)_2\text{Cl}_2$  and  $\text{Sn}(\text{C}^2\text{H}^5)_3\text{Cl}$ , the former being produced according to the equation:



Stannotriethyl, treated with stannic chloride, yields stannotriethyl chloride and metallic tin:



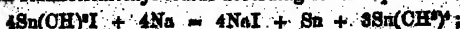
*Stannotriethyl ethylate*,  $\text{Sn}(\text{C}^2\text{H}^5)_2(\text{OC}^2\text{H}_5)_2$ , is formed by the action of sodium ethylate on stannotriethyl iodide, the mixture being ultimately heated to  $200^\circ$  with reversed condenser, and then distilled out of contact with air. It is a colourless liquid having a very unpleasant odour, boiling at  $190^\circ$ – $192^\circ$ , burning with a bright flame and separation of tin, and separating silver from an alcoholic solution of the nitrate. Sp. gr. = 1.2834 at  $0^\circ$ . Treated with iodine, it yields two compounds, one boiling at  $240^\circ$ , the other at a higher temperature. With water it forms crystals having the properties of the stannotriethyl hydrate described by Löwig & Cahours (v. 829). This hydrate boils at  $269^\circ$ – $273^\circ$ , melts at  $43^\circ$  and changes when left over sulphuric acid, the melting point rising by nearly  $100^\circ$  (Ladenburg).

*Stannomethyls*. Ladenburg's observations on the stannomethyl-compounds differ considerably from those of Cahours (v. 832), according to which the action of methyl iodide on sodium stannide produces stannodimethyl or stannous methide,  $\text{Sn}(\text{CH}_3)_2$ , and stannotetramethyl or stannic methide,  $\text{Sn}(\text{CH}_3)_4$ . Ladenburg, following the directions given by Cahours, obtained, after distilling off the ether, only a few drops of residue (probably containing stanno-dimethyl), but found that the ether distilled off contained a compound which could not be purified by fractional distillation. He therefore altered the process so far as to heat sodium stannate, containing 14 p.c. of tin, with three-fourths of its weight of methyl iodide, first in the water-bath, then to  $120^\circ$  in the oil-bath, and afterwards in the sand-bath, and subject the product to fractional distillation, whereupon it separated into stannotetramethyl and stannotrimethyl iodide.

*Stannotetramethyl or Stannic Methide*,  $\text{Sn}(\text{CH}_3)_4$ , (freed from iodide by repeated fractional distillation over sodium) is a colourless liquid, having an ethereal odour, insoluble in water, boiling at  $78^\circ$  (at  $140^\circ$  Cahours), having a sp. gr. of 1.313 at  $0^\circ$ , and vapour-density, obs. = 6.00; calc. = 6.16.

*Stannotrimethyl Iodide or Stannic Iodotrimethide*,  $\text{Sn}(\text{C}^2\text{H}_5)_3\text{I}$ . This compound is obtained, more abundantly than by the process above described, by the action of 1 mol. iodine ( $\text{I}_2$ ) on 1 mol. stannous methide,  $\text{Sn}(\text{CH}_3)_2$ . It is a liquid boiling at  $170^\circ$  and having a sp. gr. of 2.1432 at  $0^\circ$ , 2.1096 at  $18^\circ$ . (According to Cahours, it boils at  $190^\circ$  and has a sp. gr. of 2.155 at  $18^\circ$ ). From silver nitrate it first throws down silver iodide, afterwards metallic silver.

Sodium acts on stannotrimethyl iodide according to the equation:



it is possible, however, that the compound  $\text{Sn}^2(\text{CH}_3)_6$  may be formed in the first instance, and afterwards decomposed like the corresponding ethyl compound. The action of sodium ethylate on stannotrimethyl iodide produces a relatively small



quantity of stannotrimethyl ethylate, together with a large quantity of stannotetramethyl, from which mixture only the latter can be separated in the pure state.

**TITANIFEROUS IRON.** The following analyses of this mineral from Greensborough, North Carolina, have been collected by J. P. Lesley (*Proc. of the American Philosophical Society*, xii. 189): 1-3 by F. A. Genth; 4 by J. B. Britton; 5 and 6 by C. E. Buck; 7 and 8 by A. A. Fesquet.

FeO*	TiO*	MnO*	CrO*	SiO*	AlO*	CaO	MgO	H <sub>2</sub> O	X*
46.91	2.63				undetermined				—
60.03	16.08								—
79.78	12.08	0.28	0.32	0.75	4.62	0.13	2.04	—	—
84.27	4.95	—	—	—	4.81	0.24	—	1.66	3.25
83.68	8.72	0.42	0.40	1.89	3.93	0.17	1.86	—	—
81.80	12.32	trace	trace	1.04	3.87	0.64	0.49	0.34	—
83.42	8.65	0.12	0.83	1.50	2.90	0.75	2.02	—	—
79.14	13.74	0.69	trace	0.62	4.50	0.72	0.54	—	—

\* Insoluble matter mixed with the separated titanitic acid. Traces of sulphur in 4 and 6, of phosphorus in 7, of vanadium in 8.

The occurrence of titaniferous iron and magnesian iron ore in the Senfzergründel at Hinterhermsdorf in the Saxon Switzerland, is described by A. Stelzner (*Jahrbuch. f. Mineralogie*, 1871, 630). The several localities of *titaniferous magnetite sand* are enumerated by H. J. Buckart (*ibid.* ix. 421).

**TITANIUM.** On the Spectrum of titanium, see Troost a. Hautefeuille (*Compt. rend.* lxxiii. 620; *Chem. Soc. J.* [2], 1147).

On the separation of titanium from Niobium and Tantalum, see Rammelsberg (*Chem. Soc. J.* [2], x. 194).

*Titanic Oxide or Anhydride*, TiO<sub>2</sub>.—On the isomorphism of this oxide with stannic oxide, see G. Wunder (*J. pr. Chem.* [2], ii. 206).

Heated in an atmosphere of carbon monoxide, it gives up 4.7 p.c. oxygen, with separation of carbon (J. L. Bell, *Chem. News*, xxiii. 267).

On *Phosphotitanic acid*, see PHOSPHATES (p. 976).

*Titanic Oxychloride*, Ti<sup>IV</sup>O<sup>2</sup>Cl<sup>2</sup> =  $\begin{matrix} \text{Cl}^{\text{I}}\text{Ti} & \text{---} & \text{Ti} & \text{---} & \text{O} \\ | & & | & & \\ \text{Cl}^{\text{I}}\text{Ti} & \text{---} & \text{Ti} & \text{---} & \text{O} \end{matrix}$ , is formed by the direct action of oxygen on titanitic chloride, TiCl<sub>4</sub> (Troost a. Hautefeuille, *J. pr. Chem.* [2], 4, 298).

**TOBACCO.** The physiological action of tobacco when used as a narcotic has been examined by Vohl a. Eulenberg (*Arch. Pharm.* [2], cxlvii. 130; *Chem. Soc. J.* [2], ix. 1075), with especial reference to the constituents of tobacco smoke. From the chemical history of tobacco they conclude that its action cannot be attributed to the narcotine which it contains, and this conclusion they confirm by analyses and experiments of their own.

The amount of nicotine in snuff was found to be only from .0392 to .062 p.c.; in the strongest tobacco for chewing there was only a trace of nicotine, and in other specimens of the same kind there was none at all, so that nothing like nicotine-poisoning can result from the use of these tobaccos.

The smoke of strong tobacco containing 4 p.c. of nicotine was also analysed, part of it being burned in a pipe and part as cigars. The smoke was drawn by an aspirator, first through potash-solution to collect acids, and then through dilute sulphuric acid to collect bases. Besides this, the gases given off when cigars were smoked were collected and examined. These consisted of oxygen, nitrogen, carbonic oxide, and marsh-gas.

The potash-solution was found to have absorbed hydrocyanic, sulphydric, formic, acetic, propionic, butyric, valeric and carboic acids; the presence of caproic, caprylic and succinic acid was doubtful. An oily liquid collected on the surface of the potash-solution, which solidified to a buttery mass, and this, when distilled, yielded at first a small quantity of hydrocarbons of the benzene-series, not, however, including benzene itself, and at higher temperatures a substance which solidified on cooling, and, after pressure and several recrystallisations from ether, had the form of viscerous scales melting at 64°-65°; it boiled above the range of the mercurial thermometer, and agreed in percentage composition, and in the characters of its picric acid compound, with the hydrocarbon C<sup>10</sup>H<sup>18</sup>, obtained by Kraus from wood-tar and examined by Fehling and by Fritzsche (*Jahrb. f. Chem.* 1858, 439, 440).

The dilute sulphuric acid was found to have absorbed the whole series of bases of

the pyridine series, viz. *pyridine*,  $C^4H^5N$ , *picoline*,  $C^4H^5N$ , *lutidine*,  $C^5H^6N$ , *collidine*,  $C^5H^6N$ , *parvoline*,  $C^5H^6N$ , *coridine*,  $C^5H^6N$ , *rubidine*,  $C^5H^6N$ , and *viridine*,  $C^5H^6N$ . When the tobacco is smoked in the form of cigars, the greater portion of the bases contained in the tobacco consists of collidine, which appears to be identical with the base called *aldehydine* by Baeyer (1st Suppl. 82). The most minute examination of the bases of tobacco-smoke failed to detect any trace of nicotine. All the volatile bases actually found, excepting ammonia and traces of ethylamine, belonged to the pyridine series; but it is possible that pyrrol bases may also be present.

The fact that very strong tobacco, which can scarcely be smoked in pipes, may be used for making cigars, is explained by the abundant occurrence of the highly volatile and intoxicating pyridine in pipe-smoking, whereas cigar-smoking produces only a small quantity of pyridine, but a large quantity of collidine. In general, pipe-smoking produces a larger proportion of the more volatile bases.

To determine the physiological action of the bases contained in tobacco-smoke, Eulenberg a. Vohl made experiments with pigeons and rabbits on the action of the more and less volatile picoline or pyridine bases from tobacco-smoke, from *Taraxacum officinale*, willow wood, and *Datura stramonium*. From these experiments it appears that all picoline bases are very poisonous, and differ from one another only in the rapidity and intensity of their action.

Vohl a. Eulenberg are of opinion that the disagreeable symptoms felt by persons beginning to smoke, and the chronic affections which occur in those who smoke to excess, as well as the cases of poisoning from swallowing tobacco-juice, are due, not to nicotine, but to the pyridine and picoline bases. The idea that they were due to nicotine originated in the fact that picoline bases having a high boiling point, such as parvoline, resemble that alkaloid greatly both in smell and in physiological action.

**TOLANE**,  $C^{10}H^{10}$  (1st Suppl. 1099). This hydrocarbon is formed, together with barium sulphate, by heating barium benzoate with sulphur:



The tolane may be purified by repeated distillation over finely divided lead, or by heating its ethereal solution with lead or copper, and rectifying. It is also produced by heating a mixture of benzoate and sulphocyanate of barium (Pfankuch, *J. pr. Chem.* [2], iv. 35; vi. 113).

Tolane dissolves with brown colour in fuming sulphuric acid, and when heated, likewise in ordinary sulphuric acid, forming tolane-sulphonic acid, the barium and calcium salts of which are also brown, very soluble in water, and uncrystallisable. On heating either of these salts with potash, and adding hydrochloric acid to the fused mass, sulphurous oxide is evolved, and ether then extracts from the mass a brown oil containing benzoic acid and phenol (Limpricht a. Schwanert, *Deut. Chem. Ges. Ber.* iv. 379; *Jahresb. f. Chem.* 1871, 459).

**Tolane Alcohol**,  $C^{10}H^{10}O^2$ , is formed, together with benzoic, and acetic acids, by the action of alcoholic potash on acetyl-benzoïn,  $C^{10}H^{11}(C^2H^3O)^2$  (i. 559). (Jena a. Limpricht, *Ann. Ch. Pharm.* clv. 89). It is not produced by fusing tolane-sulphonic acid with potash (Limpricht a. Schwanert).

**Tolane Chlorides**. *Tolane tetrachloride*,  $C^{10}H^6Cl^4$ , is formed by the action of phosphorus pentachloride at  $200^\circ$  on chlorobenzile,  $C^{10}H^{10}OCl^2$  (1st Suppl. 308). In boiling alcoholic solution it is easily converted by sodium-amalgam into tolane (Zinin, *Zeitschr. f. Chem.* [2], iv. 718). Treated in alcoholic solution with *sine*, it yields the two isomeric dichlorides,  $C^{10}H^8Cl^2$ , already described (p. 167), one melting at  $153^\circ$ , the other at  $63^\circ$  (Zinin). Limpricht a. Schwanert (*loc. cit.*) state that they have obtained the same two tolane dichlorides by heating 1 mol. tolylene (stilbene) to  $170^\circ$  with 2 mols. phosphorus pentachloride and a small quantity of the oxychloride. They confirm Zinin's statement respecting the melting points and solubilities of these bodies and their reactions with sodium-amalgam. They also find that both, when heated to  $180^\circ$  with alcoholic potash, yield tolane, together with potassium chloride; that their ethereal solution when evaporated leaves the compound  $C^{10}H^8OCl^2$  unaltered; that each of these isomeric chlorides when distilled is partly converted into the other, a transformation which likewise takes place on heating them to  $300^\circ$  with glacial acetic acid and silver acetate, no acetyl-derivatives being thereby produced. Tolane treated with phosphorus pentachloride yields yellowish needles melting at  $137^\circ$ – $145^\circ$ , and white glassy prisms melting at  $150^\circ$ , both of which appear, from the chlorine determination, to have the composition  $C^{10}H^8Cl^2$  (Limpricht a. Schwanert).

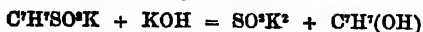
**Tolane Bromides**. Tolane likewise forms with bromine two isomeric bromides,  $C^{10}H^8Br^2$ , one of which, crystallising in scales and melting at  $200^\circ$ – $203^\circ$ , has already been described by Limpricht a. Schwanert (1st Suppl. 1099), the other, melting at  $84^\circ$ .

by Jena. Each of them, when heated to 170°–180° with water for several hours, is partly converted into the other. By distillation the modification melting at 64° is converted into that which melts at 200°–205°, whilst the latter, under the same circumstances, undergoes scarcely any alteration. By alcoholic potash or sodium-amalgam both modifications are converted into tolane. When continuously heated with water to 200° and above, both yield benzile, tolane, and hydrogen bromide. Heated to 120° with glacial acetic acid and silver acetate, they yield, together with benzile and tolane, white crystals of the compound  $C^{11}H^{14}(C^2H^3O)Br$ , melting at 107°; but if the temperature is allowed to rise to 140°–150°, the only products are benzile and tolane (Limpricht & Schwanert).

**TOLIDINE**,  $C^{11}H^{13}N$ . See next page.

**TOLUENE**,  $C^6H^8 = C^6H^7.CH^3$ . This hydrocarbon is formed in small quantity, together with products of higher boiling point, by heating potassium phenate with potassium acetate (Pfankuch, *J. pr. Chem.* [2], iv. 35).

*Conversion into Cresol*.—Toluene treated with sulphuric acid yields two isomeric tolueno-sulphonic acids, the potassium salts of which, when decomposed by melting potash, yield the corresponding cresols, one liquid, the other solid at ordinary temperatures, melting at 34.5°, and boiling at 202°:



(Wurtz, *Ann. Chim. Phys.* [4], xxv. 108).

*Reaction with Iodine*.—Toluene heated with iodine to 250° yields hydriodic acid, benzene, a hydrocarbon boiling at about 140° (xylene?), benzyltoluene,  $C^{11}H^{14}$  (p. 183), and products boiling above 130°. The latter when distilled yield viscid hydrocarbons not yet examined, and a red solid residue, from which absolute alcohol extracts a red amorphous substance melting at about 100°, and having a composition represented by the formula  $nC^{11}H^{11}$  (Schützenberger, *Compt. rend.* lxxv. 1767).

**Azotoluene**,  $C^{11}H^{11}N$ . This compound, discovered by Wergo & Jaworsky (1st *Suppl.* 285), has been further examined by F. Melms (*Deut. Chem. Ges. Ber.* iii. 549), who confirms the previous statements respecting its melting point, solubility, &c. It dissolves easily in fuming nitric acid, the solution after some time depositing small yellow crystals of a nitro-compound melting at 190.5°. It dissolves readily also in strong sulphuric acid, and is separated by water in its original state. It is soluble in water, alcohol, and dilute acids, but does not decompose carbonates. On mixing it with alkalis, the corresponding salts separate out, the sodium salt in yellow leaflets, the ammonium salt in yellow needles. Azotoluene is easily dissolved by bromine. By ammonium sulphide or sodium-amalgam it is converted into hydrazotoluene.

According to Petrieff (*Zeitschr. f. Chem.* vi. 264), nitric acid of sp. gr. 1.5, added to azotoluene in a cooled vessel, converts it into mononitro-azotoluene,  $C^{11}H^{11}(NO^2)N$ ; but if added, without cooling, it forms trinitro-azotoluene,  $C^{11}H^{11}(NO^2)_3N$  and trinitro-azoxytoluene,  $C^{11}H^{11}(NO^2)_2N^2O$  (1st *Suppl.* 285).

**Azoxytoluene**,  $C^{11}H^{11}N^2O$ , is formed in small quantity, together with azotoluene, by the action of sodium-amalgam on nitrotoluene in alcoholic solution. According to Melms, the best yield of it is obtained by using only 6 pts. alcohol to 1 pt. of nitrotoluene. It crystallises, according to Melms, in yellow needles melting at 70°; according to Petrieff, in large red laminae melting at 57°. It is insoluble in water, dilute acids, and alkalis, easily soluble in alcohol and ether, decomposed by heat into azotoluene and toluidine. With strong nitric acid it forms nitro-derivatives. By strong sulphuric acid it is first dissolved, and afterwards partially decomposed. From its solution in fuming sulphuric acid, water throws down a red resinous mass. Bromine acts strongly on it, producing bromazoxytoluene,  $C^{11}H^{11}BrN^2O$ , which crystallises from them in small light yellow tablets melting at 74° (Melms).

**Hydrazotoluene**,  $C^{11}H^{11}N^2$ , is formed from azotoluene or azoxytoluene by the action of sodium-amalgam or ammonium sulphide. In contact with alcohol and air it is quickly reoxidised to azotoluene, and it is best prepared by heating azotoluene to 100° in sealed tubes with a saturated alcoholic solution of ammonium sulphide; it then separates in crystals which may be purified by washing with water (Melms).

Hydrazotoluene forms large colourless plates or needles, which melt at 124° and are resolved at high temperatures into azotoluene and toluidine. It is insoluble in water, easily soluble in alcohol, ether, and benzene; the solutions soon turn yellow from formation of azotoluene, and on addition of an acid this decomposition takes place immediately (Melms). By slow oxidation of an alcoholic solution of hydrazotoluene, azoxytoluene is produced as well as azotoluene (Petrieff).

**Tolidine**,  $C^{11}H^{13}N$ . This base, isomeric with hydrazotoluene, and homologous

with bensedine,  $C^{12}H^{12}N^2$ , is formed by the action of sulphurous acid on hydrazotoluene (Melms), or by dropping strong hydrochloric or sulphuric acid into an alcoholic solution of hydrazotoluene prepared with sodium-amalgam, the corresponding salt being then obtained; hydrazotoluene prepared with ammonium sulphide does not yield it (Petrieff). The free base forms colourless silvery laminae, easily soluble in boiling water, alcohol, and ether; melting at  $128^{\circ}$ – $129^{\circ}$ , and decomposing when strongly heated (Petrieff). According to Melms, the crystals turn yellow or brownish on drying, and melt with brown coloration at  $103^{\circ}$ .

With sulphuric acid tolidine forms two salts, one soluble in hot water and alcohol, the other insoluble; the formula of the latter is  $C^{14}H^{14}N^2 \cdot 2H^2SO^4$ . The hydrochloride,  $C^{14}H^{14}N^2 \cdot 2HCl$ , is easily soluble in water, insoluble in hydrochloric acid, ether, and alcohol. Its aqueous solution forms, with platonic chloride, a yellow crystalline precipitate (Petrieff), dark red according to Melms. The picrate forms reddish-yellow needles (Melms).

**Bromotoluenes.** 1. *Monobromotoluene*,  $C^8H^7Br \cdot CH^3$ .—The para- and ortho-modifications of this compound, which are formed simultaneously by the direct action of bromine on toluene (1st Suppl. 280), have been further examined by Hübner a. Retschy (*Zeitschr. f. Chem.* [2], vii. 618).

Parabromotoluene is obtained by repeated crystallisation from alcohol, and careful pressure, in splendid crystals melting at  $28^{\circ}$ – $29^{\circ}$ , and resolidifying at  $28^{\circ}$ ; it boils constantly at  $185^{\circ}$ – $2^{\circ}$ . On dissolving it in 3 or 4 vols. of fuming sulphuric acid at a temperature not exceeding  $80^{\circ}$ , it yields two isomeric bromotoluene-sulphonic acids, which may be separated in the form of barium salts.

*Orthobromotoluene*.—To obtain this compound in the pure state, the crude liquid, forming about half of the total product of the action of bromine on toluene, was cooled down to  $-20^{\circ}$ . On adding a few pieces of calcium chloride, some crystals of the para-compound separated. The liquid was poured off, and twice cooled down for some hours to  $-21^{\circ}$ , when some more of the solid compound crystallised out. After seven fractional distillations, the liquid boiled at  $183^{\circ}$ – $2^{\circ}$ , but it still contained a little of the para-compound, which was removed by acting on the liquid bromotoluene with a mixture of manganese dioxide, sulphuric acid, and glacial acetic acid, the parabromotoluene being oxidised to parabromobenzoic acid, whilst a part of the orthobromotoluene was completely destroyed, resembling in this respect orthonitrotoluene, which, like the bromo-compounds, does not give on oxidation a substituted benzoic acid.

Pure orthobromotoluene is a limpid liquid, boiling at  $181^{\circ}$ – $182^{\circ}$ , not acted upon by sodium in the cold. On dissolving it at a gentle heat in Nordhausen sulphuric acid, it yields only one sulpho-acid.

Dmochowsky (*Deut. Chem. Ges. Ber.* v. 333) separates liquid from solid bromotoluene by repeatedly boiling the liquid expressed in the cold with chromic acid mixture as long as parabromobenzoic acid is thereby formed. There then remains a considerable quantity of liquid bromotoluene, which is not converted into an acid by oxidation.

*Metabromotoluene* is prepared from metabromotoluidine by Griess's method. The conversion of the metaluidine into diazotoluidine must be performed by small portions at a time, on account of the violence of the action. The liquid perbromide decomposed with alcohol yields metabromotoluene in the form of a liquid of sp. gr. 1.401 at  $18^{\circ}$ , boiling at  $182^{\circ}$ – $183^{\circ}$ , and not solidifying at  $-20^{\circ}$ . By oxidation with chromic acid it is converted into a resin from which no acid can be extracted. Bromine converts it into liquid dibromotoluene. It yields three sulpho-acids, distinguished as  $\alpha$ ,  $\beta$ , and  $\gamma$  (Wroblevsky, *Zeitschr. f. Chem.* [2], vii. 609).

*Parabromotoluene* dissolved in ether or in light petroleum oil is converted by sodium into ditolyl,  $(C^8H^7)^2$  (Zincke, *Deut. Chem. Ges. Ber.* iv. 398; Longuinine, *ibid.* 614). Orthobromotoluene dissolved in light petroleum oil is not attacked by sodium at ordinary temperatures, but when a mixture of equal volumes of orthobromotoluene and petroleum oil is heated with sodium to  $50^{\circ}$  for about six days, toluene is formed, together with smaller quantities of crystals, and an oil distilling between  $272^{\circ}$  and  $277^{\circ}$  (Longuinine).

As sodium acts strongly at ordinary temperatures ( $15^{\circ}$ ) on parabromotoluene, but not on the liquid ortho-modification, it may be used to purify the latter from any portion of the solid modification that may remain in it after refrigeration. For this purpose the liquid bromotoluene, dissolved in three times its volume of petroleum oil, is treated at ordinary temperatures with sodium as long as the metal is thereby altered. Orthobromotoluene thus purified boils at  $180^{\circ}$ – $5^{\circ}$ – $181^{\circ}$  (Longuinine).

Orthobromotoluene, treated with sodium and methyl iodide, is converted into orthoxylylene (Jannasch a. Hübner, *Zeitschr. f. Chem.* [2], vii. 796).

*Dibromotoluene*,  $C^H^4Br^2 = C^H^3Br^2.OH^1$ . Several modifications of this compound have been obtained by Wroblevsky (*Zeitschr. f. Chem.* [2], vi. 239; vii. 136, 209, 271). Bromotoluidine from solid (para-) toluidine was converted into the azoperbromide,  $C^H^4Br.N^2Br^2$ , and the latter was decomposed by alcohol. With alcohol of 80 p.c. orthobromotoluene was obtained; with alcohol of 94 p.c. the product consisted of three-fourths  $C^H^4Br^2$ , and one fourth  $C^H^3Br^2$ . The dibromotoluene,  $C^H^4Br^2.Br.OH^1$ , thus obtained is a liquid which does not solidify at  $-20^\circ$  and boils at  $238^\circ-239^\circ$ . Sp. gr. = 1.812 at  $19^\circ$ . By nitration, it yields a nitrodibromotoluene,  $C^H^4(NO^2)Br^2$ , which crystallises in beautiful needles melting at  $86^\circ-87^\circ$ , and when treated with tin and hydrochloric acid, is converted into a dibromotoluidine which crystallises in nacreous scales melting at  $95^\circ$ , and does not combine with acids.

Dibromotoluene,  $C^H^4Br^2.Br$ , obtained by brominating orthobromotoluene, remains fluid at  $-20^\circ$ , boils at  $236^\circ$ , and has a sp. gr. of 1.8127 at  $19^\circ$ ; it is not oxidised by chromic acid. The nitrodibromotoluene obtained from it crystallises in needles, which melt at  $86^\circ-87^\circ$ , and yield a dibromotoluidine which separates in silky prismatic crystals melting at  $83^\circ$ . The same dibromotoluene is obtained by the action of absolute alcohol on the perbromide,  $C^H^4Br.N^2Br^2$ , from orthobromometatoluidine.

When the dibromotoluidines prepared from meta- and para-toluidine are introduced into alcohol saturated in the cold with nitrous acid, they are converted into isomeric dibromotoluenes. The reaction takes place in the cold, yielding nearly the theoretical quantity of dibromotoluene, together with aldehyde. The dibromotoluene thus prepared from metatoluidine is nearly insoluble in water and not very soluble in alcohol, melts at  $42.5^\circ$  and boils at  $239^\circ$ . By nitration it yields a dibromonitrotoluene,  $C^H^4Br^2(NO^2)$ , crystallising from alcohol, in which it is not very soluble, in beautiful needles melting at  $59^\circ$ . The dibromotoluene prepared from paratoluidine crystallises readily from alcohol in long needles, melts at  $60^\circ$  and boils at  $241^\circ$ . By nitration it yields a dibromonitrotoluene easily soluble in alcohol, and separating therefrom in prismatic needles which melt at  $124^\circ$ . These two dibromotoluenes are isomeric with that which Fittig obtained by direct action of bromine on toluene at ordinary temperatures (*1st Suppl.* 280), and with the two previously obtained by Wroblevsky (*supra*). Wroblevsky regards it as probable that the one obtained from paratoluidine has the orientation, 1 : 2 : 6; that from metatoluidine 1 : 2 : 5.

Dibromorthotoluidine,  $C^H^4Br^2.(NH^2)$ , yields, by elimination of  $NH^2$ , a dibromotoluene,  $C^H^4Br^2$ , which has a sp. gr. of 1.812 at  $22^\circ$ , remains fluid at  $-20^\circ$ , boils at  $246^\circ$ , and smells like monobromotoluene. By nitration it is converted into  $C^H^4(NO^2)Br^2$ , which crystallises from benzine in prisms melting at  $79^\circ$ .

All the six isomeric dibromotoluenes possible according to Kekule's orientation theory are therefore known; their properties are exhibited in the following table:

*Dibromotoluenes.*

	$C^H^4Br^2$	Melting point	Boiling point	Specific gravity	$C^H^4Br^2(NO^2)$ m. p.	$C^H^4Br^2(NH^2)$ m. p.
From toluene:	m-p 1 : 3 : 4	$107^\circ-108^\circ$	$245^\circ$	—	—	—
From dibromo-paratoluidine:	o-o 1 : 2 : 6 (?)	$60^\circ$	$241^\circ$	—	$124^\circ$	$73^\circ$ (?)
From dibromo-metatoluidine:	o-m 1 : 2 : 5 (?)	$42.5^\circ$	$239^\circ$	—	$59^\circ$	$80^\circ$ (?)
From orthobromotoluene and orthobromometatoluidine:	o-m 1 : 2 : 3 (?)	Liquid	$238^\circ-239^\circ$	1.812 (at $19^\circ$ )	$86^\circ-87^\circ$	$83^\circ$
From dibromorthotoluidine:	m-m 1 : 3 : 5	Liquid	$246^\circ$	1.812 (at $22^\circ$ )	$79^\circ$	$92.5^\circ$ (?)
From orthobromoparatoluidine:	o-p 1 : 2 : 4	Liquid	$237^\circ$	1.8127 (at $19^\circ$ )	$86^\circ-87^\circ$	$95^\circ$

*Isodetoluene*,  $C^H^4I = C^H^3.I.OH^1$ .—*Orthiodetoluene* is prepared from orthotoluidine by converting the nitrate of that base into diazotoluene and decomposing the

latter with hydriodic acid. It is a light yellow liquid which boils at  $205^{\circ}$ , and has a sp. gr. of 1.697 at  $20^{\circ}$ . It is not converted into an acid by boiling with chromic acid. By nitration it yields two nitro-products, one solid, the other liquid. The solid modification forms small, thin, yellow needles melting at  $98^{\circ}$ – $99^{\circ}$  (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* iii. 102).

By treating mercury-ditolyl with iodine, Dreher a. Otto (*Ann. Ch. Pharm.* cliv. 171) have obtained an iodotoluene different from the preceding and from that which Körner obtained by decomposing sulphate of diazotoluene (para-) with hydriodic acid (1st Suppl. 284). It boils between  $200^{\circ}$  and  $210^{\circ}$ , and solidifies in large rhombic plates smelling like anise, and melting a little above  $20^{\circ}$ . It dissolves easily in alcohol, ether, and carbon sulphide, and volatilises with vapour of water.

**Chloriodotoluenes.**—Wroblevsky (*Zeitschr. f. Chem.* [2], vi. 164) has prepared two isomeric compounds,  $C^7H^4ClI$ , from the diazo-derivatives of the two chlorotoluidines.  $\alpha$ -Chloriodotoluene boils at  $242^{\circ}$ – $243^{\circ}$ , has a sp. gr. of 1.716 at  $17^{\circ}$ , and does not solidify at  $-14^{\circ}$ .  $\beta$ -Chloriodotoluene boils at  $240^{\circ}$ , has a sp. gr. of 1.770 at  $19.5^{\circ}$ , and solidifies at  $+10^{\circ}$ .

**Para-iodo-orthobromotoluene**,  $C^7H^4I_2Br$ , likewise prepared by Wroblevsky, by decomposing the diazo-compound of orthobromoparatoluidine, is a liquid which does not solidify at  $-14^{\circ}$ , boils at  $265^{\circ}$ , and has a sp. gr. of 2.044 at  $20^{\circ}$ .

**Nitrotoluenes** (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2], v. 280, 521, 529; Rosenstiehl, *Ann. Chim. Phys.* [4], xxvii. 433–476). *Para*- and *orthonitrotoluenes* are obtained by the action of nitric acid (sp. gr. 1.475) on toluene. On submitting the product to distillation, the whole of that which passes over above  $230^{\circ}$  solidifies in the cold; this is *paranitrotoluene*. When purified by recrystallisation from alcohol it melts at  $54^{\circ}$  and boils at  $235^{\circ}$ – $236^{\circ}$  (B. a. K.); melts at  $52^{\circ}$  and boils at  $237^{\circ}$ – $238^{\circ}$  (Rosenstiehl). It is almost insoluble in water, but dissolves readily in alcohol, ether, and liquid nitrotoluene. When pure it is converted by the further action of nitric acid into dinitrotoluene, but when mixed with a large portion of the liquid modification, it is oxidised by nitric acid (Rosenstiehl).

**Orthonitrotoluene**.—According to Beilstein a. Kuhlberg, this liquid modification may be completely separated from *paranitrotoluene* by repeated rectification; according to Rosenstiehl the separation is never complete. Beilstein a. Kuhlberg also prepare this modification from dinitrotoluene by converting this base into nitrotoluidine, and the latter by treatment with nitrous acid in presence of alcohol (Griess's method) into mononitrotoluene. Orthonitrotoluene thus prepared boils at  $222^{\circ}$ – $223^{\circ}$ , has a sp. gr. of 1.163 at  $23.5^{\circ}$ , agreeing therein with the liquid nitrotoluene prepared directly from toluene. According to Rosenstiehl, when purified as far as possible by fractional distillation, it still retains 3.76 p.c. of the solid modification, and the liquid so far purified boils at  $219^{\circ}$ – $220^{\circ}$ . It is not oxidised by chromic acid mixture. It is the modification analogous in constitution to Rosenstiehl's pseudotoluidine.

**Metanitrotoluene** is prepared by Beilstein a. Kuhlberg as follows: When the acetyl-compound of solid toluidine (acetotoluidine) is added by small portions to well-cooled nitric acid of sp. gr. 1.475 as long as any action is perceptible, the liquid poured into snow, and the precipitate, after washing with water, repeatedly crystallised from hot water, nitroacetotoluidine,  $C^7H^4(NO^2)(NH^2.C^2H^3O)CH^3$ , is obtained in splendid lemon-yellow, glassy needles melting at  $02^{\circ}$ . By treating this compound with alcoholic potash, precipitating with water, and recrystallising from alcohol,  $\gamma$ -nitrotoluidine,  $C^7H^4(NO^2)N$ , is obtained in small red prisms melting at  $114^{\circ}$ . Lastly, by drenching this compound with strong nitric acid, passing nitrous acid into the liquid, and further treating it according to Griess's process, *metanitrotoluene* is obtained as a liquid having a sp. gr. of 1.168 at  $22^{\circ}$ , boiling at  $230^{\circ}$ – $231^{\circ}$ , solidifying in a freezing mixture, and then melting at  $+16^{\circ}$ . By oxidation with chromic acid mixture it is easily converted into (ordinary) *metanitrobenzoic acid*.

**Dinitrotoluene**,  $C^7H^4(NO^2)_2$ .—By prolonged agitation of *metanitrotoluene* with very strong nitric acid,  $\gamma$ -dinitrotoluene is obtained in long, slender, colourless needles melting at  $60^{\circ}$ . 100 pts. of carbon sulphide at  $16^{\circ}$  dissolve 219 pts. of this body. Ordinary dinitrotoluene, formed by heating toluene with fuming nitric acid or treating it with a mixture of strong nitric and sulphuric acids (i. 575), has the same solubility, but melts at  $70.5^{\circ}$ .

**Trinitrotoluene**,  $C^7H^3(NO^2)_3$ , is obtained by boiling toluene with a mixture of fuming nitric and sulphuric acids. It forms white flat needles very much like dinitrotoluene, melting at  $82^{\circ}$ , easily soluble in ether and in hot alcohol, more easily in concen-

\* Called in Beilstein a. Kuhlberg's paper *metanitrotoluene*; but the prefix 'meta' is there applied to 1 : 2 derivatives; 'ortho' to 1 : 3 derivatives.

posed by hot alkalis than the dinitro-compound (Wilbrand, *Ann. Ch. Pharm.* cxxviii. 178).

The same compound (b. p.  $76^{\circ}$ – $82^{\circ}$ ) appears to be obtained by boiling metanitrotoluene with fuming nitric and sulphuric acids; 100 pts. of carbon sulphide at  $19^{\circ}$  dissolve 0.236 pt. of it. By the action of ammonium sulphide it is converted into nitro-diamidotoluene or nitrotolylene-diamine,  $C_6H_4(NO^2)(NH^2)_2$ , and dinitrotoluidine,  $C_6H_4(NO^2)_2NH^2$  (Beilstein a. Kuhlberg).

**НИТРОБРОМОТОЛУЕНА,  $C_6H_4Br(NO^2)$ .**—According to Wroblevsky a. Kurbatow (*Zeitschr. f. Chem.* [2], vii. 165), solid bromotoluene yields by nitration two isomeric nitrobromotoluenes. *α*-Nitrobromotoluene crystallises from alcohol in long needles, melts at  $43^{\circ}$ , boils at  $256^{\circ}$ – $257^{\circ}$ , and yields a liquid bromotoluidine solidifying at  $-2^{\circ}$ . *β*-Nitrobromotoluene is liquid, boils at  $256^{\circ}$ – $256^{\circ}$ , does not solidify at  $-20^{\circ}$ , has a sp. gr. of 1.631 at  $18^{\circ}$ , and yields a solid bromotoluidine melting at  $67^{\circ}$ .

Heynemann (*Zeitschr. f. Chem.* [2], vi. 402) obtains parabromometanitrotoluene,  $C_6H_4Br(NO^2)$ , by converting ordinary dinitrotoluene into nitrotoluidine, the nitrate of this base into diazotoluene by the action of nitrous acid, and decomposing the sulphate of diazotoluene with hydrobromic acid. It dissolves easily in ether and carbon sulphide, melts at  $43^{\circ}$ , boils at  $256^{\circ}$ – $257^{\circ}$ , agreeing therein with Wroblevsky's *α*-nitrobromotoluene; but the parabromometoluidine prepared from it differs from Wroblevsky's *α*-bromotoluidine in being solid at ordinary temperatures, and melting at  $30^{\circ}$ . This bromotoluidine dissolves in 111.1 pts. of water at  $17^{\circ}$ .

**НИТРОДИХЛОРОТОЛУЕНА,  $C_6H_3(NO^2)Cl_2$ ,** prepared by nitration of dichlorotoluene (b. p.  $196^{\circ}$ – $200^{\circ}$ ), solidifies completely at low temperatures like nitrobenzene, boils at  $274^{\circ}$ , and has a sp. gr. of 1.455 at  $17^{\circ}$ . By reduction it yields dichlorotoluidine,  $C_6H_3(NH^2)Cl_2$ , in dazzling white elongated laminae melting at  $88^{\circ}$  and boiling at  $259^{\circ}$  (Wroblevsky a. Pirogow, *Zeitschr. f. Chem.* [2], vi. 164).

**НИТРОДИОТОЛУЕНА,  $C_6H_4I(NO^2)$ , or  $C_6(CH_3)HHI(NO^2)H$ ,** prepared like the corresponding bromine compound, is a faintly yellowish, well-crystallised compound, which dissolves easily in ether and carbon sulphide, melts at  $60.5^{\circ}$ – $61^{\circ}$ , sublimes even at this temperature in slender capillary crystals, and begins to boil with decomposition at  $286^{\circ}$ . By reduction with tin and hydrochloric acid it is converted into paraiodorthotoluidine, which forms colourless needle-shaped crystals, melts at  $48^{\circ}$ – $49^{\circ}$ , and boils with rapid decomposition at  $273^{\circ}$  (Heynemann, *loc. cit.*)

**TOLUENESULPHONIC ACID,  $C_6H_5SO^3 = C_6H_5\begin{Bmatrix} CH^3 \\ SO^3H \end{Bmatrix}$**  (Engelhardt a.

Latschinoff, *Zeitschr. f. Chem.* v. 617; Anna Wolkow, *ibid.* vi. 321; *Jahresb. f. Chem.* 1870, 741). Two of these acids, the *para* or *α*, and the *ortho* or *β* modification, are formed by heating toluene on the water-bath with an equal weight of fuming sulphuric acid. They are separated by converting them into potassium salts, the *α* salt first crystallising out pure as the solution cools, and the mother-liquor on further concentration yielding a second crop of the *α*-salt mixed with nodules of the *β*-salt. Engelhardt a. Latschinoff separate these salts by sifting, the more soluble *β*-salt passing through with the mother-liquor. Wolkow picks out the crystals of the *α*-salt, recrystallises the remainder, again picks out the *α*-salt, &c., and finally recrystallises the nodular *β*-salt.

**Tolueneparasulphonic Acid,  $C_6H_4(CH_3)SO^3H$ .** The potassium salt,  $C_6H_4KSO^3 + H^2O$ , crystallises in large, long, six-sided tables and prisms, or by rapid cooling in long needles. It dissolves in hot alcohol and crystallises therefrom in needles; the crystals effloresce on exposure to the air (Engelhardt a. Latschinoff). On fusing it with potassium hydrate, and decomposing the mass with hydrochloric acid, it yields paroxybenzoic acid—as previously observed by Barth with crude toluene-sulphonate of potassium (*Deut. Chem. Ges. Ber.* ii. 523)—together with paracresol (Wolkow).

The other salts are prepared by liberating the acid with sulphuric acid, dissolving in alcohol, and neutralising. The sodium salt crystallises from alcohol in shining leaflets. The barium salt,  $(C_6H_4SO^3)_2Ba$ , is soluble in boiling alcohol, and crystallises therefrom in shining leaflets. The calcium salt crystallises from alcohol in needles. The lead salt dissolves easily in water, and crystallises in nodular groups of needles (Engelhardt a. Latschinoff).

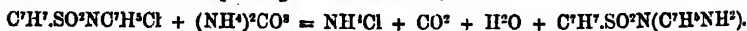
**Tolueneparasulphochloride,  $C_6H_4(SO^2Cl)_2$ ,** is obtained by heating the potassium salt on the water-bath with an equal weight of phosphorus pentachloride, treating the mass with water, and recrystallising the residuum from ether. It forms rhombic tables melting at  $69^{\circ}$ ; slowly decomposed by water, and is doubtless identical with the chloride previously described by Fittig, Märcker, Jaworsky, and Otto (v. 358).

*Tolueneparasulphamide*,  $C^6H^4(SO^2NH_2)$ , is formed by gently heating the chloride with strong aqueous ammonia. It crystallises from water and alcohol in shining laminae, melting at  $137^\circ$ . It possesses acid properties, dissolves in aqueous ammonia and potash more easily than in water, and is not decomposed by strong aqueous or alcoholic potash. When evaporated down with aqueous potash (1 mol. of the amide to 1 mol. KHO) it forms a compound which may be dissolved out by alcohol, and crystallises on evaporation in silky needles (Wolkow).

The *paratoluide* of the  $\alpha$ -acid,  $C^6H^4(SO^2NHC^6H^5)$ , is formed by the action of the parasulphochloride on paratoluidine, these substances being heated together on the water-bath till the reaction is finished, the product boiled with water containing hydrochloric acid, and the residue crystallised from alcohol. It forms large shining crystals melting at  $117^\circ$ , and slightly soluble in water (Wolkow).

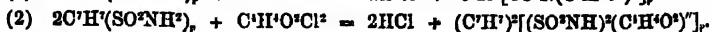
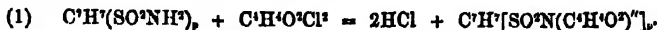
*Tolueneparasulphobenzamide*,  $C^6H^4[SO^2NH(C^6H^5O)]$ , is formed by the action of benzoyl chloride on tolueneparasulphamide at  $150^\circ$ – $160^\circ$ . The product, purified by treatment with ether and recrystallisation from boiling alcohol, forms four-sided transparent flat prisms or needles, melts at  $147^\circ$ – $150^\circ$ , dissolves easily in boiling alcohol, sparingly in cold alcohol, very sparingly in ether and in boiling water. The solutions have an acid reaction, and decompose carbonates. Silver nitrate and barium chloride form white precipitates with the ammoniacal solution. The *potassium salt*,  $C^6H^4[SO^2NK(C^6H^5O)]$ , crystallises from boiling alcohol in laminae. The *barium salt*,  $(C^6H^5)^2[SO^2N(C^6H^5O)]^2Ba$ , is slightly soluble in water, and crystallises therefrom in stellate groups of needles. The *calcium salt*,  $(C^6H^5)^2[SO^2N(C^6H^5O)]^2Ca + H^2O$ , crystallises in nodules easily soluble in water and in alcohol. The *silver salt*,  $C^6H^4[SO^2NAg(C^6H^5O)]$ , is a white precipitate nearly insoluble in water, easily soluble in ammonia. The ammoniacal solution when left to evaporate yields needles of the *argentammonium salt*,  $C^6H^4[SO^2N(NH^4Ag)(C^6H^5O)]$ , (A. Wolkow, *Zeitschr. f. Chem.* [2], vi. 577).

Tolueneparasulphobenzamide, treated with *phosphorus pentachloride*, is converted (by exchange of HO for Cl) into the chlorinated amide,  $C^6H^4(SO^2NC^6H^5Cl)$ , which crystallises from ether and melts at  $100^\circ$ . This chlorinated amide is converted by water into the original acid amide by exchange of Cl for HO, and by ammonium carbonate into the corresponding neutral amide, thus:



This neutral amide crystallises from alcohol, melts at  $140^\circ$ , is insoluble in water, aqueous ammonia, and alkaline carbonates; caustic alkalis dissolve it slowly, with evolution of ammonia (A. Wolkow).

*Tolueneparasulphosuccinamides*.—Tolueneparasulphamide treated with succinyl chloride yields two amides formed by the action of 1 mol. succinyl chloride on 1 or 2 mols. tolueneparasulphamide:



The first is an anhydride very slightly soluble in ether and crystallising therefrom in four-sided prisms. It unites with ammonia, forming the monobasic acid,  $N^1(C^6H^4SO^2)(C^4H^3O^2)^1H$  or  $C^6H^4O^2 \begin{matrix} \text{NH} - C^6H^4SO^2 \\ \text{NH}^2 \end{matrix}$ , whose salts have the

composition  $N^1(C^6H^4SO^2)(C^4H^3O^2)^1H^2M$ . It unites also with water, forming the bibasic acid,  $N^2(C^6H^4SO^2)(C^4H^3O^2)^2H^2O$ , whose salts have the composition  $N^2(C^6H^4SO^2)(C^4H^3O^2)^2M^2O$ .

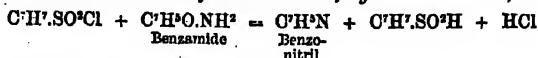
The second amide is a bibasic acid, which crystallises from hot alcohol in flat needles. Its solution in strong ammonia forms with *silver nitrate* and *barium chloride* white precipitates, containing respectively  $(C^6H^4)^2(SO^2NAg)^2(C^4H^3O^2)$  and  $(C^6H^4)^2(SO^2NBa)(C^4H^3O^2)$  (A. Wolkow, *loc. cit.*)

**Toluenecorthosulphonic Acid ( $\beta$ -acid).** The potassium salt of this acid, separated in the manner already described (p. 1167), is far from pure. It crystallises from alcohol in small laminae containing  $C^6H^4(SO^2K) + 1\frac{1}{2}H^2O$ , and when treated with phosphorus pentachloride yields the solid chloride already described and a liquid chloride. The former, heated with alcoholic potash, yields the  $\alpha$ -potassium salt, the latter the  $\beta$ -salt, which crystallises from alcohol in laminae, and is converted by phosphorus pentachloride into the liquid chloride. Perfectly pure  $\beta$ -compounds can, however, be prepared only by decomposing the  $\beta$ -amide—which can be obtained quite free from the  $\alpha$ -amide—with nitrous acid. The  $\beta$ -acid is thereby produced, and the salts may be prepared from it by neutralisation.



$\beta$ -Toluenesulphonic acid belongs to the ortho-series.\* Its potassium salt fused with potash yields salicylic acid, and a liquid cresol boiling in a stream of carbon dioxide at  $188^{\circ}$ – $190^{\circ}$  (orthocresol, see 1st Suppl. 507). The  $\beta$ -potassium salt,  $C^6H^7(SO^2K) + H^2O$ , crystallises from water in nodules, from alcohol in shining plates which lose their water over oil of vitriol (Wolkow). The barium salt,  $(C^6H^7SO^2)Ba + x aq.$ , dissolves easily in boiling water and crystallises in nodules (Engelhardt & Latschinoff).

*Toluene-orthosulphochloride*,  $C^6H^7(SO^2Cl)_2$ .—This chloride, heated with benzamide, succinamide, and acetamide, yields the corresponding nitrils, together with toluene-orthosulphonic acid and hydrochloric acid; e.g.:



(A. Wolkow, *Zeitschr. f. Chem.* [2], vi. 421).

*Toluene-orthosulphamide*,  $C^6H^7(SO^2NH^2)_2$ , prepared from the chloride by the action of ammonia and recrystallised from hot alcohol, forms shining octohedral crystals, sparingly soluble in boiling water; it melts at  $153^{\circ}$ – $154^{\circ}$ , and exhibits slightly acid properties. It dissolves in ammonia more readily than in water, also in aqueous potash, which does not decompose it at the boiling heat. Heated with boiling alcoholic potash, it yields the compound  $C^6H^7(SO^2NHK) + \frac{1}{2}H^2O$ , which crystallises in laminae (Wolkow).

*Toluene-orthosulphobenzamide*,  $C^6H^7[SO^2NH(C^6H^5O)]_2$ , is formed by the same process as the para-compound (p. 1168), but the yellowish syrupy product does not crystallise on cooling, but merely becomes thicker. To purify it, the mass is drenched with ether-alcohol, which dissolves it and converts the unaltered benzoyl chloride into benzoic ether; the crystalline mass remaining on evaporation is dissolved in sodium carbonate, and the solution, after being filtered to remove the benzoic ether, is precipitated with hydrochloric acid. The amide thus obtained forms a tenacious white precipitate which solidifies after a while to a crystalline mass. After washing with water and recrystallisation from ether, it forms transparent tablets and prisms, melting at  $110^{\circ}$ – $112^{\circ}$ , slightly soluble in water, easily in alcohol and ether. Like the para-compound it reddens litmus and decomposes alkaline carbonates.

The *potassium salt*,  $C^6H^7[SO^2NK(C^6H^5O)] + \frac{1}{2}H^2O$ , forms spherical groups of needles very soluble in water and in alcohol. The *barium salt*,  $[C^6H^7SO^2N(C^6H^5O)]^2Ba + H^2O$ , crystallises in flat prisms; the *calcium salt* is anhydrous and crystallises after strong concentration in spherical groups of needles easily soluble in water and in alcohol. The *silver salt*, also anhydrous, is a white precipitate sparingly soluble in water, freely in ammonia (A. Wolkow, *Zeitschr. f. Chem.* [2], vi. 57).

*Paranitrotoluene-orthosulphobenzamide*,  $C^6H^4(NO^2)_2[SO^2NH(C^6H^5O)]_2$ , is obtained by heating equivalent weights of  $\beta$ -nitrosulphotoluene-amide and benzoyl chloride to  $145^{\circ}$ – $150^{\circ}$  as long as hydrochloric acid is given off. It crystallises in flat prisms grouped in stars, melts at  $130^{\circ}$ , and is readily soluble in boiling alcohol, but only sparingly in ether and boiling water. Its solution has an acid reaction, and decomposes alkaline carbonates. The *potassium salt*,  $C^6H^4(NO^2)_2[SO^2NK(C^6H^5O)]_2$ , is anhydrous, readily soluble in water and alcohol, and forms warty needles. The *barium salt* is insoluble in alcohol, sparingly soluble in water, and forms needles grouped in stars. The *calcium salt* crystallises from water and alcohol in nodules. The *silver compound* is a precipitate drying up to a horny mass, slowly attacked by boiling with hydrochloric acid (A. Wolkow, *ibid.* 422).

This amide, heated to  $145^{\circ}$ – $150^{\circ}$  with phosphorus pentachloride, is converted (by exchange of HO for Cl) into the chlorinated amide,  $C^6H^4(NO^2)_2(SO^2NC^6H^5Cl)$ , which dissolves sparingly in boiling ether, and crystallises therefrom, melts at  $122^{\circ}$ – $123^{\circ}$ , and dissolves slowly in aqueous alkalis, with evolution of ammonia.

*Toluenemetasulphonic Acid*,  $C^6H^7(SO^2H)$ , is prepared by the action of sodium-amalgam on the sodium salt of the bromotoluenesulphonic acid obtained by treating crude bromotoluene with strong sulphuric acid, after it has been freed from solid bromotoluene. The liquid, after six days' action, is saturated with sulphuric acid; the greater part of the sodium sulphate removed by concentration; the mother-liquor evaporated to dryness; the residue treated with phosphorus pentachloride; and the resulting toluenesulphochloride is washed and decomposed by heating it with water to  $130^{\circ}$ . On evaporating the resulting solution till the temperature rises to  $110^{\circ}$ , and passing a rapid stream of air through it at this temperature as long as hydrochloric acid continues to escape, metatoluenesulphonic acid remains as a brownish syrup which

\* In the original memoir it is said to be a meta-compound; but at the time when that memoir was published (1870), salicylic acid was also regarded as belonging to the meta-series.

solidifies to a crystalline mass on cooling. The following salts are extremely soluble in water and alcohol, and agree in their amounts of crystallisation-water with the corresponding bromotoluenesulphonates:

$C^6H^4SO^2K$	$+ \frac{1}{2}H^2O$	Highly lustrous laminae, resembling naphthalene.
$C^6H^4SO^2Na$	$+ \frac{1}{2}H^2O$	Crystallises from alcohol in large, shining laminae.
$(C^6H^4SO^2)^2Ba$	$+ 2H^2O$	Non-crystalline powder.
$(C^6H^4SO^2)^2Ca$		Separates from alcohol in small shining tablets.
$(C^6H^4SO^2)^2Pb$	$+ 2H^2O$	Separates from water in rosettes of laminae; from absolute alcohol in long needles, and is precipitated from the alcoholic solution by ether in small shining tablets. Gives off its water at $130^\circ$ , and is then very hygroscopic.

*Metatoluenesulphochloride*,  $C^6H^4SO^2Cl$ , prepared from the potassium salt by the action of phosphorus pentachloride, is a clear faintly-yellow liquid, having a pungent odour, not solidifying at  $-10^\circ$ , insoluble in water, easily decomposed by heating it with water in a sealed tube to  $130^\circ$ .

*Metatoluene sulphhydrate*,  $C^6H^4SH$ , formed by the action of tin and hydrochloric acid on the sulphochloride, is a limpid, strongly refracting liquid, having a powerful odour, and exerting a caustic action on the skin. It does not solidify at  $-10^\circ$ , is insoluble in water, easily soluble in alcohol, dissolves sulphur and iodine, and forms sparingly soluble compounds with metals.

*Metatoluene disulphide*,  $(C^6H^4)^2S^2$ , produced by boiling the sulphhydrate for several days with strong nitric acid, is a yellowish oil which remains fluid at  $-12^\circ$ , boils, with decomposition, at about  $150^\circ$ , is insoluble in water, but easily soluble in alcohol, ether, and xylene. Strong nitric acid converts it into a brown resinous mass.

*Metatoluenesulphamide*,  $C^6H^4SO^2.NH^2$ , obtained by boiling the chloride with aqueous ammonia, evaporating, and exhausting with ether, is a crystalline body moderately soluble in cold, easily in boiling water, very easily in alcohol, ether, and ammoniacal water. From a slightly concentrated solution it crystallises at low temperature in small threadlike forms, from a more concentrated solution at  $30^\circ$  in transparent, colourless tables of the size of a square inch; if the temperature falls below  $20^\circ$ , the first form appears. Melts at  $91^\circ-92^\circ$ .

The above-described characters of this sulpho-acid and its derivatives, especially of the chloride and amide, show that it is quite distinct from para- and ortho-toluenesulphonic acid, and must therefore be the meta-compound.

#### Toluenedisulphonic Acid, $C^6H^4(SO^2H)^2 = C^6H^4 \begin{pmatrix} OH \\ (SO^2H) \end{pmatrix}$ Senhofer

(*Ann. Ch. Pharm.* cxliv. 126) obtains an acid of this composition by heating toluene with Nordhausen sulphuric acid and phosphorus pentoxide for four or five hours to  $230^\circ$ . On opening the tubes a large quantity of sulphur dioxide is evolved. The brown residue is dissolved in water, and the solution is boiled and neutralised with barium carbonate. By adding alcohol to the concentrated filtrate, the *barium salt* is obtained as a white precipitate, having the composition  $C^6H^4(OH)(SO^2)^2Ba + 3\frac{1}{2}H^2O$ . The *potassium salt* is produced by adding milk of lime to a solution of the crude acid and precipitating the calcium salt with potassium carbonate. By recrystallisation, it is obtained in short, well-defined prisms, having the composition  $C^6H^4(OH)(SO^2)^2K + H^2O$ .

By decomposing the barium salt with sulphuric acid, evaporating the filtrate, and exhausting the residue with a mixture of alcohol and ether, a solution of the *free acid* is obtained, crystallising in a vacuum over sulphuric acid in soft microscopic needles.

The *silver salt*,  $C^6H^4(OH)(SO^2Ag) + 2H^2O$ , is formed by neutralising a boiling solution of the acid with silver oxide; it forms yellow crystals. The *cadmium salt* is a gum-like mass; the *ammonium salt* forms very soluble needles.

By fusing the potassium salt with potash, salicylic acid and isoeurin,  $C^6H^4O^2$ , are produced. The latter compound melts at  $87^\circ$ , boils at  $260^\circ$ , and solidifies on cooling to a radiate crystalline mass. It has a faint sweet taste, and dissolves in water, alcohol, and ether. Isoeurin has great resemblance to orcin, from which, however, it

differs by its reactions. Its solution does not assume a red colour when exposed to the air; with ferric chloride it yields a brownish-green colour; it reduces ammoniacal silver solutions even in the cold, and gives, with bleaching powder, a red colour changing gradually into yellow. In presence of ammonia and air it acquires a brown colour, but becomes colourless again on addition of acetic acid.

Potassium toluenedisulphonate, fused with sodium formate, is converted into the potassium salt of isoxylidic acid,  $C^6H^4(CH^3)(CO^2H)^2$ . This acid is almost insoluble in cold water, sparingly soluble in hot water, but readily in alcohol and ether, and forms microscopic crystals. When heated, it begins to soften at  $280^\circ$ , but melts only completely at  $375^\circ$ . By sublimation it is obtained in yellowish well-defined needles. The barium salt,  $C^6H^4(CH^3)(CO^2)Ba + 2H^2O$ , is a yellowish crystalline mass; the silver, lead, cadmium, and copper salts are amorphous precipitates.

Two other toluenedisulphonic acids ( $\alpha$  and  $\beta$ ) have been obtained by P. Hakansson (*Deut. Chem. Ges. Ber.* v. 1084), by heating toluenemonosulphonic acid (which ?) with fuming sulphuric acid to about  $160^\circ$ . Both appear to differ from Senhofer's acid ( $\gamma$ -acid). The following are the chief points of difference between the  $\alpha$ - and  $\beta$ -acids.

$\alpha$ -Toluenedisulphonic chloride,  $C^6H^4(SO^2Cl)^2$ , crystallises from ether in large four-sided prisms, which melt at  $51^\circ$ – $52^\circ$ ; the  $\beta$ -chloride is less soluble in ether, has apparently a different crystalline form, and melts at  $94^\circ$ . The  $\alpha$ -amide,  $C^6H^4(SO^2NH^2)^2$ , crystallises in thin long prisms which melt at  $186^\circ$ ; the  $\beta$ -amide is less soluble in water and melts at  $216^\circ$ . The  $\alpha$ -chloride, boiled with an alkaline sulphite, yields toluenedisulphonic acid,  $C^6H^4(SO^2H)^2$ . The  $\alpha$ -acid, fused with potash, yields, together with salicylic acid and small quantities of paraoxybenzoic acid, a body having the composition  $C^7H^5O^4$ , but differing in its properties both from ordinary orcin and from Senhofer's isocin.

The  $\alpha$ -acid, fused with sodium formate, yields a small quantity of a toluene-dicarboxylic acid,  $C^6H^4(CO^2H)^2$ , in the form of white difficultly soluble flocculi, which exhibit signs of melting below  $270^\circ$ , but are at the same time carbonised.

The potassium salt of the  $\alpha$ -disulpho-acid, digested with chromic acid mixture, is slowly oxidised and converted into  $\alpha$ -disulphobenzoic acid,  $C^6H^4(CO^2H)(SO^2H)^2$ , which is different from the acid obtained by Barth & Senhofer directly from benzoic acid (*Ann. Ch. Pharm.* clix. 217); it yields a highly characteristic, difficultly soluble, acid potassium salt,  $C^6H^4(CO^2H)(SO^2K)^2 + H^2O$ , which is precipitated on the addition of hydrochloric acid to a solution of the normal potassium salt,  $C^6H^4(CO^2K)(SO^2K)^2 + 2H^2O$ .

**Bromotoluenesulphonic Acids.**  $C^6H^4Br.SO^2H$ . Hübner & Retzschy (*Zeitschr. f. Chem.* [2], vii. 618; *Jahresb. f. Chem.* 1871, 501).

I. From Crystallised Parabromotoluene.—Hübner & Post (*Zeitschr.* vi. 390; *Jahresb.* 1870, 746) describe three isomeric sulpho-acids obtained by dissolving parabromotoluene in fuming sulphuric acid; but Hübner & Retzschy find that, as theory requires, only two distinct sulpho-acids are thus produced, viz.:

$\alpha$ . Parabromotoluene-orthosulphonic acid	$C^6$	$CH^3$	$SO^2H$	$H$	$Br$	$H$	$H$
$\beta$ . Parabromotoluene-metasulphonic acid	$C^6$	$CH^3$	$H$	$SO^2H$	$Br$	$H$	$H$

These acids are prepared by dissolving 1 vol. pure parabromotoluene in 3 to 4 vols. fuming sulphuric acid, with agitation, and heating to a temperature not exceeding  $80^\circ$ . The characters of their salts and derivatives are as follows:

(1).  $\alpha$ -series (Hübner & Post's  $\gamma$ -series). The barium salt,  $(C^6H^4Br.SO^2)Ba + 7H^2O$ , crystallises in long well-defined needles which do not become opaque by being left in the mother-liquor, or by exposure to sunshine. The lead salt,  $(C^6H^4Br.SO^2)Pb + 3H^2O$ , separates at first in long pointed needles, but, after repeated crystallisation, it is obtained by slow evaporation in groups of light-yellow, well-defined rhombic crystals which preserve their lustre unaltered even after prolonged exposure over sulphuric acid. The strontium salt,  $(C^6H^4Br.SO^2)Sr + 7H^2O$ , forms small rather hard crystals acid. The amide,  $C^6H^4Br.(SO^2NH^2)_2$ , prepared up of two four-sided irregular pyramids. The amide,  $C^6H^4Br.(SO^2NH^2)_2$ , prepared from the corresponding chloride  $C^6H^4Br.(SO^2Cl)_2$ , crystallises in soft needles nearly an inch long, perfectly colourless, having a silky lustre, and united in groups having exactly the appearance of a fan-shaped palm-leaf. It dissolves sparingly in cold, easily in hot water, also in alcohol and in ether. Melts at  $151^\circ$ – $152^\circ$ .

(2).  $\beta$ -series. The barium salt,  $(C^6H^4Br.SO^2)Ba + H^2O$ , crystallises very slowly from the cold saturated solution in hard whetstone-shaped crystals, apparently composed of thick rhombic prisms grouped in rosettes. From the hot solution the salt separates as an apparently amorphous mass; but on dissolving this mass in a large quantity of water, it crystallises, by slow cooling, in large, soft, flexible, silvery laminae, apparently belonging to the rhombic system. 1 pt. of this salt requires for solution

186 pts. of water at 8°. The lead salt,  $(C^6H^5BrSO^3)^2Pb + 3H^2O$ , separates gradually from its cold solution, after several hours' standing, in stellate groups of small needles which, when once formed, rapidly grow into arborescent forms. At low temperatures the salt separates very quickly in larger groups of fine soft needles; they have a satiny lustre, but when exposed to the air quickly lose part of their water and become dull. The calcium salt,  $(C^6H^5BrSO^3)^2Ca + 4H^2O$ , crystallises in thin laminae, or sometimes in groups of three-sided tablets with truncated summits. The crystals are rather hard and shining, and when left over sulphuric acid, give off part of their water and become dull.

*β-Parabromotoluenesulphamide*,  $C^6H^4Br(SO^2NA^+)_2$ , melts at 166°–167°, and crystallises from water in long shining slender needles.

II. *Orthobromotoluenesulphonic acid*.—Pure liquid bromotoluene was converted, by agitation and careful warming with fuming sulphuric acid, into the sulphonic acid, and this into the barium salt,  $(C^6H^4BrSO^3)^2Ba + 2H^2O$ , which crystallises in large soft elongated plates; no isomeric salts were found in the mother-liquor. 1 pt. of the barium salt dissolves in 253 pts. at 17°. The calcium salt,  $(C^6H^4BrSO^3)^2Ca$ , crystallises very slowly from a highly concentrated solution in thick rhombic tables, becoming hexagonal by truncation of their acute angles, and grown together by their edges. It has an extraordinary lustre, is anhydrous, and remains perfectly transparent after being heated to 186° for six hours. It is very soluble in water. The lead salt,  $(C^6H^4BrSO^3)^2Pb + 2H^2O$ , forms tufts of long narrow tables, and is much more soluble than the barium salt. The potassium salt,  $C^6H^4BrSO^3K + \frac{1}{2}H^2O$ , forms small, thick, rather hard, white needles, moderately soluble in water. The sodium salt,  $C^6H^4BrSO^3Na + \frac{1}{2}H^2O$ , crystallises in large thick rhomboidal tables with truncated edges, and is very soluble in water.

Orthobromotoluenesulphonic acid is converted, by oxidation with potassium dichromate and dilute sulphuric acid, into orthobromosulphobenzoic acid (Hübner a. Retschy).

According to Dmochowsky (*Deut. Chem. Ges. Ber.* v. 333) pure orthobromotoluene, treated with fuming sulphuric acid, yields two sulphonic acids which yield barium salts containing  $(C^6H^4BrSO^3)^2Ba + 2H^2O$ , one sparingly soluble in water, the other easily soluble. Both acids, when fused with potash, yield salicylic acid.

III. *Metabromotoluenesulphonic acids* (Wroblevsky, *Zeitschr. f. Chem.* [2], vii. 6).—When fuming sulphuric acid is added to cooled metabromotoluene, the reaction completed by warming in the water-bath, and the product saturated with baryta, three barium salts ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) are formed which may be separated by fractional crystallisation. The  $\beta$ -salt forms the largest portion of the product, next the  $\alpha$ -salt (about 25 p.c.) and of the  $\gamma$ -salt only a small quantity is obtained (3 p.c.)

The  $\alpha$ -barium salt,  $(C^6H^4BrSO^3)^2Ba + H^2O$ , crystallises in small prisms; 1,000 pts. of water at 19° dissolve 5.28 pts. of it. The  $\alpha$ -potassium salt crystallises in small prisms. By fusion with potash it yields salicylic acid: hence the  $\alpha$ -acid is metabromotoluene-orthosulphonic acid,  $C^6H^3Br(SO^3H)_2$ .

The  $\beta$ -barium salt,  $(C^6H^4BrSO^3)^2Ba + 3H^2O$ , crystallises in beautiful shining laminae. 1,000 pts. of water at 19° dissolve 14.52 pts. of this salt. The  $\beta$ -lead salt,  $(C^6H^4BrSO^3)^2Pb + 3H^2O$ , forms large prisms. The  $\beta$ -calcium salt,  $(C^6H^4BrSO^3)^2Ca + 5H^2O$ , crystallises easily in large prismatic laminae. The  $\beta$ -potassium salt crystallises in large shining laminae. This salt also yields by fusion with potash, a considerable quantity of salicylic acid, so that the  $\beta$ -sulpho-acid is likewise a metabromotoluene-orthosulphonic acid.

The  $\gamma$ -barium salt,  $(C^6H^4BrSO^3)^2Ba + 5H^2O$ , crystallises in needles. 1,000 pts. of water at 19° dissolve 32.48 pts. of it. By fusing the  $\gamma$ -potassium salt with potash, an oxy-acid was obtained, which did not colour ferric salts: therefore either oxybenzoic or para-oxybenzoic acid.

The following table, on p. 1173, gives a comparative view of the properties of the three bromotoluenes and of their sulphonic derivatives.\*

**Chlorotoluenesulphonic Acid**,  $C^6H^4Cl(SO^3H)_2$ . Two acids ( $\alpha$  and  $\beta$ )

having this composition are produced by heating chlorotoluene with sulphuric acid; their barium and potassium salts have been already described as chloro-cresylsulphites (p. 878). The  $\alpha$ -cadmium salt,  $(C^6H^4ClSO^3)^2Cd + 2H^2O$ , crystallises in flat needles.

\* This table is taken from Hübner a. Retschy's paper (*Zellisch. f. Chem.* [2], vii. 681). It will be observed that the quantities of water here assigned to the  $\beta$ -Ba- and  $\alpha$ -Ba- salts of the  $\beta$ -meta-acid and to the  $\beta$ -Ba-salt of the  $\gamma$ -acid are only half those ascribed to them by Wroblevsky (*supra*). In a note to the abstract of Hübner a. Retschy's paper in the *Abstract. f. Chem.* 1874, 566, it is stated that these quantities of water given by Wroblevsky have been corrected in a subsequent paper in the same volume of the *Zellisch. f. Chem.* (p. 768). This reference is incorrect, as the said volume (1874) contains only 786 pages. Moreover, the correction in question is not to be found in any other paper by Wroblevsky contained in the same volume.

*Bromotoluenes and their Derivatives.*

Parabromotoluene: solid; melting point, 28.5°; boiling point, 185.2°		Metabromotoluene, from acetbromotoluidine; liquid; boiling point, 182°		Orthobromotoluene: liquid; boiling point, 181°	
Bromotoluenesulphonic acids, C <sup>6</sup> H <sup>3</sup> .CH <sup>3</sup> .Br.SO <sup>3</sup> = A.					
α-series	β-series	α-series	β-series	γ-series	α-series
A <sup>2</sup> Ba + 7H <sup>2</sup> O	A <sup>2</sup> Ba + 11H <sup>2</sup> O	A <sup>2</sup> Ba + H <sup>2</sup> O	A <sup>2</sup> Ba + 1½H <sup>2</sup> O	A <sup>2</sup> Ba + 2½H <sup>2</sup> O	A <sup>2</sup> Ba + 2H <sup>2</sup> O
A <sup>2</sup> Pb + 3H <sup>2</sup> O	A <sup>2</sup> Pb + 3H <sup>2</sup> O	—	A <sup>2</sup> Pb + 3H <sup>2</sup> O	—	A <sup>2</sup> Pb + 2H <sup>2</sup> O
A <sup>2</sup> Sr + 7H <sup>2</sup> O	—	—	—	—	—
—	A <sup>2</sup> Ca + 4H <sup>2</sup> O	—	A <sup>2</sup> Ca + 2½H <sup>2</sup> O	—	A <sup>2</sup> Ca
Bromotoluenesulphamides, C <sup>6</sup> H <sup>3</sup> .CH <sup>3</sup> .Br.SO <sup>2</sup> .NH <sup>2</sup> .					
Melting point, 151.5°	166.5°	—		133.5°	
Bromobenzoic acids, C <sup>6</sup> H <sup>4</sup> .Br.COOH.					
Melting point, 251°	155°		137°		

easily soluble in water and in alcohol. The  $\alpha$ -potassium salt fused with potash yields orcin (Vogt a. Henniger, *Ann. Chim. Phys.* [4], xxv. 129).

Two *chlorobenzylsulphurous acids*, C<sup>6</sup>H<sup>4</sup>.Cl{CH<sup>2</sup>Cl  
SO<sup>2</sup>H}, metameric with the preceding, are formed by boiling chlorobenzoyl chloride, C<sup>6</sup>H<sup>4</sup>.Cl.CH<sup>2</sup>Cl, with potassium sulphite. See BENZYL-SULPHUROUS ACID (p. 186).

**Nitrotoluenesulphonic Acids, C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>){OH  
SO<sup>2</sup>H}**. (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2], v. 280, 521, 529). When paranitrotoluene (m.p. 54°) is digested for some days with fuming sulphuric acid, and the liquid is diluted with water and saturated with barium carbonate, barium paranitrotoluenesulphonate, [C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)SO<sup>2</sup>]<sup>2</sup>Ba + 3H<sup>2</sup>O, separates on cooling, in large, shining, yellow, crystalline tufts; by evaporation at ordinary temperatures it is obtained in broad, four-sided tables. The crystals give off all their water over sulphuric acid, and become milk-white when heated (even under water). 100 pts. of water dissolve 3.34 pts. of the salt at 18.6°. The *lead salt*, [C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)SO<sup>2</sup>]<sup>2</sup>Pb + 3H<sup>2</sup>O, crystallises in shining, pale-yellow tufts, which slowly give off 2 mols. water over sulphuric acid, 3 mols. at a higher temperature. 100 pts. water at 19° dissolve 15.2 pts. of the salt. The acid, treated with hydrogen sulphide in alcoholic solution, is converted into para-amidotoluenesulphonic acid, C<sup>6</sup>H<sup>4</sup>(NH<sup>2</sup>)SO<sup>2</sup>H + H<sup>2</sup>O, which forms long, broad, pale-yellowish, shining prisms giving off their water at 19°.

*Orthonitrotoluenesulphonic acid* is produced by treating orthonitrotoluene with fuming sulphuric acid (Beilstein a. Kuhlberg); also by the action of fuming sulphuric acid on nitrotolueneparasulphonic acid; it is therefore orthonitrotolueneparasulphonic acid, C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>).(SO<sup>2</sup>H), (Anna Wolkow). Its *barium salt*, [C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)SO<sup>2</sup>]<sup>2</sup> + 2H<sup>2</sup>O, forms shining scales or granular crystals much less soluble than the corresponding para-salt, 100 pts. of water at 19° dissolving only 0.57 pt. of it. The *lead salt*, [C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)SO<sup>2</sup>]<sup>2</sup>Pb + 2H<sup>2</sup>O, forms tufts of dazzling, white, slender needles, which do not give off their water over sulphuric acid; 100 pts. of water at 18° dissolve 0.77 pt. of the salt.

This nitrotoluenesulphonic acid is identical with that which was prepared by Märker, Otto and Beck (*1st Suppl.* 287).

By reduction with ammonium sulphide, it yields ortho-amidotolueneparasulphonic acid, identical with that described by Engelhardt a. Beck (*1st Suppl.* 287, 289).

*Orthonitrotolueneparasulphonic chloride*, C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)(SO<sup>2</sup>Cl), prepared in the usual way, is a heavy oil slowly decomposed by boiling water. The *amide*, C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)(SO<sup>2</sup>NH<sup>2</sup>), obtained by boiling the chloride with ammonium carbonate, and purified by recrystallisation from alcohol, forms shining crystals, and separates from hot water in needles. The *paratoluide*, C<sup>6</sup>H<sup>4</sup>(NO<sup>2</sup>)(SO<sup>2</sup>C<sup>6</sup>H<sup>4</sup>(NH<sup>2</sup>)), is prepared similarly to that from tolueneparasulphonic acid (p. 1168). It is sparingly soluble

in cold, easily soluble in hot water, and separates in shining crystals which melt at  $130^{\circ}$ – $131^{\circ}$  (Wolkow).

*Metanitrotoluenesulphonic acid*, prepared like its isomerides, forms a barium salt,  $[C^6H^4(NO^2)SO^2]^2Ba + 2H^2O$ , which crystallises in nodules, and is more soluble than the ortho-salt; 100 pts. of water at  $17.5^{\circ}$  dissolve 1.145 pt. of it. The lead salt,  $[C^6H^4(NO^2)SO^2]^2Pb + 2\frac{1}{2}H^2O$ , crystallises in small grains, and easily takes up an additional quantity of lead oxide, forming a basic salt which may be precipitated by alcohol (Beilstein a. Kuhlberg).

*Dinitrotoluenesulphonic Acid*,  $C^6H^3(NO^2)_2SO^2H$ , is produced, together with other acids, by treating a solution of toluene in fuming sulphuric acid for a considerable time with very strong nitric acid, at first in the cold, afterwards at a higher temperature. By saturating this mixture with lead oxide and repeated crystallisation, a lead salt was obtained in faintly-yellow shining scales, having the composition  $[C^6H^3(NO^2)_2SO^2]^2Pb + 3H^2O$ . It gives off  $2H^2O$  in a vacuum over sulphuric acid, the remainder when heated. 100 pts. water at  $14.5^{\circ}$  dissolve 2.64 pts. of this salt (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2], vi. 796).

*Nitrobromotoluenesulphonic Acids*,  $C^6H^3Br(NO^2)SO^2H$ . I. *Nitropara-bromotoluene-metasulphonic acid*. The barium salt of this acid is prepared by adding dehydrated and pulverised barium parabromotoluene-metasulphonate (p. 1171) to warm fuming nitric acid, decanting from precipitated barium nitrate, and evaporating. The free acid separated from it by sulphuric acid forms, when concentrated, a faintly yellow syrup which solidifies to a crystalline mass, easily soluble in water, alcohol, and ether, and crystallises by evaporation of its aqueous solution over sulphuric acid in stellate groups of small quickly deliquescent needles.

The acid and its salts have an intensely bitter taste. The salts dissolve easily in water and in alcohol, and crystallise well from water, with the exception of the calcium salt; all however, excepting the sodium salt, in microscopic though very sharply defined crystals.

$C^6H^3(NO^2)BrSO^2K$	Shuttle- or whetstone-shaped crystals.
$C^6H^3(NO^2)BrSO^2Na + 2H^2O$	Tufts of needles an inch long; less soluble than the other salts.
$[C^6H^3(NO^2)BrSO^2]^2Ca$	Small needles.
$[C^6H^3(NO^2)BrSO^2]^2Ba + 2H^2O$	From dilute solutions in hard nodules; from concentrated solution in stellate groups of short flattened needles.
$[C^6H^3(NO^2)BrSO^2]^2Pb + 2H^2O$	Crystallises like the potassium salt.

Microscopical examination of the lead, barium, and potassium salts showed that only one nitro-acid was formed by the process above described (Hübner a. Müller, *Zeitschr. f. Chem.* [2], vii. 14). It does not appear to have been decided whether the nitro-group in this acid occupies the ortho-position (2 or 6) or the meta-position (5).

*Nitro-β-metabromotoluenesulphonic acid* is easily obtained by nitrating β-metabromotoluenesulphonic acid (p. 1172); only one nitro-acid appears to be thereby produced. The barium salt,  $[C^6H^3(NO^2)BrSO^2]^2Ba + 7H^2O$ , crystallises in needles more soluble in hot than in cold water. The calcium salt,  $[C^6H^3(NO^2)BrSO^2]^2Ca + 9H^2O$ , is very soluble in water and in alcohol, and crystallises from alcohol in large prisms. The lead salt,  $[C^6H^3Br(NO^2)BrSO^2]^2Pb + 3H^2O$ , dissolves easily in water and crystallises in prisms (Wroblevsky, *Zeitschr.* [2], vii. 8).

**TOLUIC ACID**,  $C^6H^5O^2 = C^6H^4(CH^3).COOH$ . *Synthesis of Orthotoluic acid*.—Ramsay a. Fittig (*Zeitschr. f. Chem.* [2], vii. 584) have prepared this acid from toluene-orthosulphonic acid (p. 1168), by exchanging the group  $SO^2H$  for CN and boiling the resulting nitril with alcoholic potash. By distilling a mixture of the potassium salts of toluene-para-sulphonic acid and toluene-ortho-sulphonic acid with potassium cyanide, and treating the distillate of mixed nitrils with alcoholic potash, ordinary paratoluic acid, mixed with another toluic acid, was obtained. The calcium salts could not be separated by recrystallisation from water, but from 95 p.c. alcohol the isomeric calcium salt crystallised readily, leaving the paratoluic in solution. This isomeric toluate contained  $2H^2O$ , and gave an acid which crystallised in long shining needles, melting at  $102^{\circ}$ , and agreed in every respect with orthotoluic acid obtained by oxidation of orthoxylene. The nitro-acid was also prepared, and found to be identical with that obtained from orthotoluic acid.

*Metatoluic acid*.—This modification is formed when 1 mol. of the calcium salt of urtic acid is intimately mixed with 1 mol. calcium hydrate, and the mixture is heated for several hours in a lead-bath. The toluic acid separated from the product by solution in an acid and distillation with steam, is more soluble than ortho- or paratoluic

acid, and separates in needle-shaped crystals melting at  $105^{\circ}$  (Fittig, *Deut. Chem. Ges. Ber.* v. 268). By the action of sodium-amalgam on the modification of bromotoluic acid which melts at  $205^{\circ}$ – $206^{\circ}$  (prepared by oxidising bromoxylene, m. p.  $205^{\circ}$ – $208^{\circ}$ , with chromic acid), Ahrens (*Zeitschr. f. Chem.* [2], v. 102) obtained a toluic acid which, when oxidised by chromic acid, gave isophthalic acid, and therefore appeared to be metatoluic acid, but it melted at  $90^{\circ}$ – $93^{\circ}$ , that is to say, from  $12^{\circ}$  to  $15^{\circ}$  lower than Fittig's acid. To ascertain the cause of this difference, W. Ramsay prepared the acid according to Ahrens' method, and found that on recrystallising it from alcohol, two very different crystallisations were obtained, viz. druses of dull needles, and transparent crystals, the former consisting of pure paratoluic acid, the latter melting at  $105^{\circ}$ , just like the metatoluic acid prepared from uvitic acid (*Ann. Ch. Pharm.* clxviii. 263).

**Bromotoluic Acid**,  $C^6H^4Br \begin{Bmatrix} CH^3 \\ COOH \end{Bmatrix}$ . F. Landolph, (*Deut. Chem. Ges. Ber.* v. 268) has obtained an acid of this composition by oxidising bromocymene with chromic acid mixture. It is sparingly soluble in cold, more easily in hot water, from which it crystallises in thin needles or laminæ. It dissolves easily also in hot alcohol, in ether, and in chloroform. It is somewhat volatile with vapour of water, melts at  $203^{\circ}$ – $204^{\circ}$ , and sublimes in broad shining needles. Sodium-amalgam easily removes all the bromine, and converts the acid into ordinary paratoluic acid, melting at  $176^{\circ}$ . Chromic acid mixture decomposes the brominated acid, but partially, even after long boiling, and does not convert it into a bibasic acid. The *calcium salt*,  $(C^6H^4BrO^2)^2Ca + 3\frac{1}{2}H^2O$ , crystallises from hot water in arborescent needles sparingly soluble in cold water. The *barium salt*,  $(C^6H^4BrO^2)^2Ba + 4H^2O$ , is similar but less soluble.

This bromotoluic acid dissolves slowly in warm concentrated nitric acid, and the solution diluted with water deposits bromonitrotoluic acid,  $C^6H^3(NO^2)Br \begin{Bmatrix} CH^3 \\ COOH \end{Bmatrix}$ , which separates from water in needle-shaped crystals. It is soluble in alcohol, ether, and benzene, and does not volatilise with water-vapour. During fusion at about  $170^{\circ}$ – $180^{\circ}$  it decomposes and turns brown. The *barium salt*, which crystallises from hot dilute alcohol in stellate groups of needles, has the composition  $(C^6H^3(NO^2)BrO^2)^2Ba + H^2O$ .

The bromotoluic acid above described agrees nearly in its properties and those of its salts with that which was obtained by Fittig, Ahrens a. Mattheides from coal-tar xylene (*1st Suppl.* 1100). Nevertheless the two can scarcely be identical, since the last-mentioned acid was converted by reduction into isophthalic acid, whereas that prepared from bromocymene was converted by similar treatment into paratoluic acid.

**Alpha-toluic or Phenylacetic Acid**,  $CH^3(C^6H^4).COOH$ . This acid, when nitrated, behaves like cinnamic acid (p. 348), forming *para*- and *orthophenylacetic acid*, which latter is converted by oxidation into orthonitrobenzoic acid, shown by the degree of solubility of its barium salt, and by the fact that when reduced by tin and hydrochloric acid, it yields anthranilic acid, which may be converted into salicylic acid (Pirogoff, *Deut. Chem. Ges. Ber.* v. 332).

**Toluidine**,  $C^6H^4N = C^6H^4.NH^2 = C^6H^4(NH^2).CH^3$ . Three modifications of this base are known, *para*, *meta*, and *ortho*, formed by reduction of the corresponding nitrotoluenes. Their characteristic properties and reactions have been studied especially by Beilstein a. Kuhlberg (*Ann. Ch. Pharm.* clvi. 66; clviii. 341; *Zeitschr. f. Chem.* [2], v. 532; vi. 102, 417; vii. 99; *Jahrb. f. Chem.* 1870, 764; 1871, 712; 1872, 647), and by Wroblevsky (*Zeitschr.* [2], vii. 135, 210, 271, 609; *Jahresb.* 1871, 713; 1872, 649).

**Paratoluidine**,  $C^6H^4(NH^2).CH^3$ , is the ordinary solid modification, discovered by Hofmann a. Muspratt, and produced by reduction of solid nitrotoluene.

**Metatoluidine**,  $C^6H^3(NH^2).CH^3$ , is obtained by the action of tin and hydrochloric acid on the metanitrotoluene discovered by Beilstein a. Kuhlberg.

**Orthotoluidine**,  $C^6H^3(NH^2).CH^3$  (Rosenstiehl's *Pseudotoluidine*), is produced from the liquid modification of nitrotoluene, formed, together with solid paranitrotoluene, by direct nitration of toluene (Beilstein a. Kuhlberg); apparently also by the following processes:—

a. From *para*-amidotoluic acid, by distillation with soda-lime (Beilstein a. Kuhlberg).  
 b. By treating monobromotoluene (m. p.  $26.4^{\circ}$ ) with strong, well-cooled-nitric acid, reducing the resulting nitrobromotoluene with tin and hydrochloric acid, and debrominating the bromotoluidine with sodium-amalgam (Körner, *Compt. rend.* lxviii. 824; *Jahresb.* 1869, 677).

γ. By a similar series of processes from the mixture of *para*- and *orthobromotoluene* produced by the direct action of bromine on toluene (p. 1164) (Hübner a. Wallach,

*Zeitschr. f. Chem.* ii. 530; *Jahresb.* 1869, 678. See further, Rosenstiehl, *Compt. rend.* lxi. 53, 469; *Jahresb.* 1869, 679, 680).

The following table exhibits the most characteristic differences between the three isomeric toluidines and their derivatives:

*Isomeric Toluidines.*

	Para	Meta	Ortho
Toluidine {b.p. . . . .	198°	197°	197°
{sp. gr. . . . .	—	0.998 at 25°	0.998 at 25.5°
Of the nitrate, 100 pts. water dissolve . . .	17.7 pts. at 23.5°	20.1 pts. at 23.5°	10.01 pts. at 19.2°
Of the nitrate, 100 pts. alcohol (89 p.c.) dissolve . . .	42   "   20°	—	23.5   "   16.5°
Of the hydrochloride, 100 pts. water dissolve . . .	22.9   "   11°	—	37.4   "   15.5°
Of the hydrochloride, 100 pts. alcohol (89 p.c.) dissolve . . .	25   "   17°	—	100 pts. . .
Of the oxalate, 100 pts. water dissolve . . .	0.87   "   14°	—	2.38 pts. at 21°
Of the oxalate, 100 pts. alcohol (84 p.c.) dissolve . . .	0.48   "   22°	—	2.68   "   21°
Of the oxalate, 100 pts. ether dissolve . . .	0	—	0.65   "   21°
Of the sulphate, 100 pts. water dissolve . . .	5.06 pts. at 22°	—	7.8   "   22°
Of the sulphate, 100 pts. alcohol (89 p.c.) dissolve . . .	1.3   "   23°	—	1.6   "   21.5°
The acetyl-derivative boils at . . .	306°	303°	296°
The acetyl-derivative melts at . . .	145°	65.5°	107°
1,000 pts. water dissolve of it . . .	0.886 pt. at 22°	4.4 pts. at 13°	8.5 pts. 19°
Colour produced by toluidine with chloride of lime and hydrochloric acid . . .	none	violet	violet
Colour produced by toluidine with sulphuric and nitric acid . . .	blue	none	none

**Bromotoluidines.** Wroblevsky a. Kurbatow (*Zeitschr. f. Chem.* [2], vi. 165) have obtained two bromotoluidines,  $\alpha$  and  $\beta$ , by reduction of the two nitrobromotoluenes formed by nitration of solid bromotoluene (p. 1167).  *$\alpha$ -Bromotoluidine* is a liquid which solidifies at  $-2^\circ$ . Its nitrate forms macroscopic crystals, of which 1,000 pts. of water at  $11.5^\circ$  dissolve 8.27 pts.  *$\beta$ -Bromotoluidine* forms prismatic crystals melting at  $67^\circ$ . Its nitrate also crystallises in prismatic forms; 1,000 pts. of water at  $11.5^\circ$  dissolve 4.6 pts. of it. Heynemann (*Zeitschr.* [2], vi. 402) has obtained a base which he designates as *parabromometatoluidine*, by reduction of the corresponding bromonitrotoluene; it melts at  $80^\circ$ , but does not easily resolidify. 9 pts. of the nitrate dissolve in 1,000 pts. water at  $17^\circ$ .

**Metabromotoluidine.**  $C_6H_4Br \cdot (NH_2)_2$ , either  $C_6OH^2 \cdot NH_2 \cdot Br \cdot H \cdot H$  (1 : 2 : 3) or  $C_6CH^2 \cdot NH_2 \cdot H \cdot H \cdot Br \cdot H$  (1 : 2 : 5). Wroblevsky (*Zeitschr.* vii. 146) prepares this compound as follows. Crude toluidine is mixed with rather more than the theoretical quantity of glacial acetic acid, and boiled for 16 hours in a flask with upright tube, to separate the para- and ortho-modifications; the uncombined toluidine is separated from the solidified (the greater) portion by distillation, and this toluidine is heated for three days with the required quantity of glacial acetic acid. *Acetanilide*



toluide is thus obtained as a solid body which, however, melts not at  $105^{\circ}$ , but at  $98^{\circ}$ . By suspending it in water and dropping bromine into the liquid, bromacetoluide,  $C^6H^4Br(NH.C^2H^3O)$ , is produced, which, when purified, crystallises in long shining needles melting at  $156^{\circ}$ – $157^{\circ}$ , and dissolving easily in alcohol and in boiling water. This acetyl-compound, decomposed by alcoholic potash, yields metabromorthotoluidine, which, after distillation with steam, is solid, and crystallises in fine large octohedrons. It melts at  $57^{\circ}$ , and boils, with complete decomposition, at about  $240^{\circ}$ ; it dissolves easily in alcohol, very sparingly in water. Its hydrochloride, nitrate, and sulphate,  $(C^6H^4BrNH^2)SO^4 + 1\frac{1}{2}H^2O$ , are all soluble in water and crystallise well. The nitrate, decomposed with nitrous acid and alcohol, yields metabromotoluene, which boils at  $182^{\circ}$ , and is oxidised by chromic acid solution to meta- (ordinary) bromobenzoic acid, melting at  $153^{\circ}$ . The perbromide,  $C^6H^4Br.NH^2.Br^2$ , decomposed with absolute alcohol, yields orthometadi-bromotoluene,  $C^6H^4Br^2$  (1 : 2 : 3) or (1 : 2 : 5).

*Orthobromometatoluidine*,  $C^6H^4Br.(NH^2)_{\infty}$  (1 : 2 : 3 or 1 : 2 : 5), is obtained by the action of potash on orthobromometacetoluide, which is formed by treating metacetoluide with bromine. It is a liquid boiling at  $240^{\circ}$ , and smelling very much like ordinary toluidine. Its *nitrate* crystallises in small, reddish, sparingly soluble prisms. When it is converted into the diazo-compound, and the corresponding perbromide is decomposed by absolute alcohol, dibromotoluene,  $C^6H^4Br_2$ , is formed as a solid melting at  $42.5^{\circ}$  and boiling at  $249^{\circ}$  (Wroblevsky, *Zeitschr.* [2], vii. 609).

*Dibromotoluidines*.—1. *Dibromorthotoluidine*,  $C^6H^4Br^2(NH^2)_{\infty}$ , is produced by passing bromine (4 at.) into an aqueous solution of the hydrochloride of orthotoluidine. The base separated by lime crystallises in beautiful nacreous needles easily soluble in alcohol, nearly insoluble in water, melting at  $50^{\circ}$ . It does not combine with acids (Wroblevsky, *Zeitschr. f. Chem.* [2], vii. 210).

2. Acetometatoluide, treated with bromine in presence of water, yields dibrom-acetometatoluide,  $C^6H^4Br^2.NH.C^2H^3O$ , which forms flat needles melting at  $164^{\circ}$ , and converted, by decomposition with alkali, into dibromometatoluidine,  $C^6H^4Br^2.(NH^2)_{\infty}$ . This compound crystallises in silky needles melting at  $92.5^{\circ}$ ; does not unite with acids. By removing the amidogen groups from this dibromotoluidine, a dibromotoluene,  $C^6H^4Br^2$ , is obtained having the constitution 1 : 3 : 5 (see table, p. 1176).

3. The dibromotoluidine obtained by reduction of the nitro-dibromotoluene produced by nitration of para-orthodibromotoluene (p. 1165), crystallises in nacreous scales melting at  $95^{\circ}$ , and does not combine with acids (Wroblevsky, *Zeitschr.* [2], vi. 239).

4. The dibromotoluidine obtained from the nitrodibromotoluene formed by nitration of ortho-metadibromotoluene, forms silky prismatic crystals melting at  $83^{\circ}$  (Wroblevsky, *loc. cit.*)

*Tribromotoluidine*,  $C^6H^4Br^3.NH^2$ , is formed by passing bromine-vapour (4 at.) into the hydrochloric acid solution of metatoluidine, and separates in white flocks which may be purified by distillation with vapour of water. It dissolves sparingly in alcohol, and crystallises therefrom in long needles melting at  $97^{\circ}$ . It does not unite with acids. On adding it to alcohol saturated with nitrous acid, a violent action takes place, resulting in the formation of tribromotoluene,  $C^6H^4Br^3$ . Metatoluidine differs therefore from para- and orthotoluidine in yielding, by bromination, a tribrominated instead of a dibrominated product (Wroblevsky, *loc. cit.*)

*Chlorotoluidines*. Orthonitrotoluene, reduced with tin and hydrochloric acid, yields a chlorotoluidine,  $C^6H^4Cl(NH^2)$ , which melts at  $29.5^{\circ}$ , boils at  $241^{\circ}$ , dissolves easily in alcohol, ether, and carbon sulphide. Its *hydrochloride* forms thin white crystals. The *nitrate* forms large thin quadrangular striated crystals, of which 100 pts. water at  $19^{\circ}$  dissolve 3.712 pts. By conversion into the diazo-compound, and decomposition of this compound with hydriodic acid, a chloridotoluene is obtained boiling at  $240^{\circ}$  (Beilstein a. Kühlberg, *Zeitschr. f. Chem.* vi. 102).

*Dichlorotoluidine*,  $C^6H^4Cl^2.NH^2$ .—The nitrodichlorotoluene produced by nitration of the dichlorotoluene, which boils at  $195^{\circ}$ – $200^{\circ}$ , yields, by reduction, a dichlorotoluidine which forms dazzling white, elongated laminae, melts at  $88^{\circ}$ , and boils at  $250^{\circ}$  (Wroblevsky a. Pirogow, *Zeitschr.* [2], vi. 164).

*Iodotoluidine*. *Para-iodorthotoluidine*,  $C^6H^4I.(NH^2).CH^3$ , prepared by reduction of para-iodorthonitrotoluene (p. 1167), forms needle-shaped colourless crystals which melt at  $48^{\circ}$ – $49^{\circ}$ , and boil, with rapid decomposition, at  $273^{\circ}$ . It dissolves very easily in alcohol, ether, and carbon sulphide. The *nitrate* crystallises from hot water in colourless nacreous laminae. 1000 pts. of water at  $16^{\circ}$  dissolve 9.5 pts. of this salt. The *diazo-compound*, which is formed from it with difficulty, is decomposed by water, even at ordinary temperatures, yielding dinitro-iodocresol,  $C^6H^3(HO)(NO^2)_2.CH^3$ ,

which separates in slender yellow needles melting at  $75^{\circ}$ , and exploding at a higher temperature. Caustic soda dissolves this dinitrocresol, and hydrochloric acid precipitates it from the solution without alteration (Heynemann, *Zeitschr.* [2], vi. 402).

**Nitrotoluidines and Nitro-acetoluides.** *Dinitropara-acetoluide*,  $C^6H^4(NO^2)_2(NH.C^2H^3O)_n$ , is obtained by adding para-acetoluide (1 pt.) in small portions to well-cooled nitric acid (4 pts.) of  $49^{\circ}$  B.; the product is precipitated with snow, washed with water, then, after drying, with ether, and recrystallised from alcohol. It forms long, pale yellow needles, much more soluble in hot than in cold alcohol, melting at  $190-5^{\circ}$ .

*Dinitroparatoluidine*,  $C^6H^4(NO^2)_2(NH^2)_n$ , is easily obtained by boiling the acetyl-derivative with alcoholic potash; it is precipitated by water, recrystallised from benzene, and finally from boiling carbon sulphide. It crystallises in yellow needles, melts at  $168^{\circ}$ , and may be sublimed in small quantities without decomposition. It is but slightly soluble in alcohol even at the boiling heat, more soluble in benzene, especially when boiling, nearly insoluble in ether; 1000 pts. of carbon sulphide at  $18^{\circ}$  dissolve 3.2 pts. of it. It is but slowly reduced by tin and hydrochloric acid, the product being apparently, not a triamine base, but a tolyleno-diamino. Dinitrotoluidine suspended in alcohol or in strong nitric acid is not acted on by nitrous acid at ordinary temperatures, but at boiling heat the dinitrotoluidine dissolves, being probably converted into dinitrotoluene (Beilstein a. Kuhlberg, *Ann. Ch. Pharm.* clviii. 341).

*Metanitro-orthacetoluide*,  $C^6H^4(NO^2)_n(NH.C^2H^3O)_n$ , or  $C^6(CH^3)(NH.C^2H^3O)(NO^2)HHH$ , is formed by adding orthacetoluide in small portions to well-cooled nitric acid of  $45^{\circ}$  B. The product is precipitated with snow, washed with water, and recrystallised from alcohol. It is very slightly soluble in water even at the boiling heat, and crystallises therefrom in microscopic needles melting at  $196^{\circ}-197^{\circ}$ . From alcohol, in which it is more soluble, it crystallises in small lemon-yellow needles.

*Metanitro-orthotoluidine*,  $C^6H^3(NO^2)_n(NH^2)_n.CH^3$ , is obtained by heating the acetyl-derivative with a mixture of 1 vol. sulphuric acid and 3 vols. water, and precipitating with ammonia; also by boiling the acetyl-derivative with alcoholic potash. It may be purified by recrystallisation from water or from aqueous alcohol. It is very slightly soluble in boiling water, and crystallises therefrom in small lemon-yellow needles which, after drying, form a felted mass; it is easily soluble in alcohol. From its hot solution in dilute nitric acid, the free base crystallises in long, flat, yellow, shining needles melting at  $127^{\circ}-128^{\circ}$ . By nitrous acid and alcohol it is converted into metanitrotoluene (Beilstein a. Kuhlberg, *loc. cit.*)

*Orthonitrometacetoluide*,  $C^6H^4(NO^2)_n(NH.C^2H^3O)_n.CH^3$ , prepared by treating acetometatoluide with cooled nitric acid of  $46-5^{\circ}$  B., precipitating with snow, and recrystallising several times from water, forms small cubes, or when crystallised by slow evaporation, larger rhombic crystals. It dissolves easily in boiling alcohol, very sparingly in water even at the boiling heat. Melts at  $101^{\circ}-102^{\circ}$ .

*Orthonitrometatoluidine*,  $C^6H^4(NO^2)_n(NH^2)_n.CH^3$ , is formed by treating the acetyl-compound just described with the theoretical quantity of alcoholic potash. It melts at  $133^{\circ}-134^{\circ}$ . By converting this base into diazotoluene by Griess's reaction, and decomposing the sulphate of this diazotoluene with absolute alcohol, a nitrotoluene is obtained, which boils constantly at the temperature of *orthonitrotoluene* and remains liquid at  $-20^{\circ}$ . Hence, it may be inferred that the nitro group in the base and its acetyl-derivative under consideration occupies the ortho-position (Beilstein a. Kuhlberg, *Zeitschr. f. Chem.* [2], vii. 99).

**Furfurotoluidine**,  $C^6H^4O^2N^2$ . Toluidine in alcoholic solution acts but slowly on furfural; a more decided action is obtained with toluidine salts. A hot mixture of 12 pts. toluidine hydrochloride and 9 pts. toluidine dissolved in 160 pts. alcohol with 8 pts. furfural, also dissolved in 150 pts. alcohol, solidifies on cooling to small red, needle-shaped crystals of *furfurotoluidine hydrochloride*,  $C^6H^4O^2N^2.HCl$ . The *nitrate*,  $C^6H^4O^2N^2.NO^3H$ , prepared in like manner with a mixture of 14 pts. toluidine nitrate and 9 pts. toluidine dissolved in 100 pts. alcohol with 8 pts. furfural in 100 pts. alcohol, forms purple needles. *Furfurotoluidine*, prepared by triturating ether of its salts with ammonia and kneading the resulting mass with water, forms, when purified by solution in ether, a brown, amorphous, brittle mass (Stenhouse, *Ann. Ch. Pharm.* clvi. 197).

*Appendix to Furfurotoluidine*. **FURFURANILINE**,  $C^6H^4O^2N^2$ . This base, prepared in a similar manner, forms a hydrochloride which crystallises in small purple needles, insoluble in benzene, carbon sulphide, and water, quickly decomposed by boiling with dilute acids or alkalis. The *nitrate* forms similar but larger crystals. The free base

is a brown mass, the alcoholic solution of which decomposes quickly in contact with the air or on boiling, and then no longer forms crystallisable salts (Stenhouse).

**TOLUIDINES, DIMETHYLISED.** On the formation of these bases by the action of heat on trimethyl-phenylammonium iodide, see AMINES (p. 57).

**TOLUIDINE-SULPHONIC ACIDS.** II. L. Buff (*Deut. Chem. Ges. Ber.* iii. 796) has examined these acids with results nearly the same as those obtained by Malyschew (*1st Suppl.* 288). He finds that the  $\beta$ -acid, heated with potassium hydrate, yields an oily base which does not form crystallisable salts; probably oxytoluidine,  $C^6H^3(OH)(NH^2).CH^3$ .

**TOLUENE,  $C^6H^{12}$ .** Syn. with STILBENE (p. 1099).

**TOLUENE ALCOHOL, HYDRATE, and OXIDE.** See HYDROBENZOÏN and DROXYBENZOÏN, under BENZOÏN (pp. 171-176).

**TOLYL (DI-),  $C^6H^{14}$  =  $C^6H^4\{CH^3\}_2$ .** This hydrocarbon, isomeric with dibenzyl and benzyl-toluene (p. 183), is produced by the action of sodium on parabromotoluene (p. 1161).

Sodium acts very briskly on a solution of solid bromotoluene in anhydrous ether, and if the liquid is not well cooled, hydrogen is evolved and a large quantity of toluene is regenerated, the formation of which indeed cannot be completely evaded, even if the vessel is surrounded by a freezing mixture. The other products of the reaction are a large quantity of a yellow solid (not further studied), which is sparingly soluble in alcohol, and can thus be easily separated from two isomeric ditolyls which dissolve readily in alcohol. That which is present in the largest quantity is a solid, which crystallises from ether in splendid monoclinic prisms and from alcohol in white plates melting at  $121^\circ$ . The second ditolyl is a liquid, having an aromatic smell and boiling at  $283^\circ$ - $288^\circ$ .

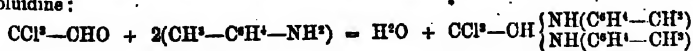
By acting with sodium on crude bromo- and chlorotoluene, only a small quantity of the solid ditolyl is obtained; the chief product is a liquid, which appears to be identical with the ditolyl (b. p.  $272^\circ$ ) which Fittig obtained (*Ann. Ch. Pharm.* cxxxix. 178) by the action of sodium on bromotoluene. That prepared from chlorotoluene boiled at  $273^\circ$ - $278^\circ$  (Zincke, *Deut. Chem. Ges. Ber.* iv. 396).

**TOLYL ISOCYANATE,  $N(CO)C^6H^7$ .** Colourless liquid boiling at  $185^\circ$ . See CYANIC ETHERS (p. 407).

**TOLYLAMINES.** *Azoditolylamine*,  $C^6H^{13}N^2$ . — Hofmann a. Geyger (*Deut. Chem. Ges. Ber.* v. 476), in attempting to prepare this base by heating toluidine to fusion on a saturated solution of common salt, and passing a rapid stream of nitrous acid through it, obtained the isomeric compound diazamidotoluene; which crystallises in lemon-yellow needles; and decomposes on boiling with hydrochloric acid into nitrogen, cresol, and toluidine:



*Trichlorethylidene-ditolylamine*,  $C^6H^{11}Cl^3N^2 = CCl^3.CH(NHC^6H^7)^2$  (Wailach, *Deut. Chem. Ges. Ber.* v. 252).—A base produced by the action of chloral on toluidine:



The reaction is attended with rise of temperature, and the mass, which solidifies on cooling, crystallises from ether in transparent prisms which melt at  $114^\circ$ - $115^\circ$ , but are decomposed by continued heating to  $100^\circ$ . It cannot be distilled.

*Trichlorethylidene-oxethyltolylamine*,  $CCl^3-CH \begin{Bmatrix} OC^2H^5 \\ NH(C^6H^4-CH^3) \end{Bmatrix}$ . If in the preparation of the preceding compound a little alcohol be added to the product while still warm, this oxethyl-compound is obtained, chiefly from the mother-liquor, in large tabular crystals very easily soluble in alcohol and ether. It crystallises with great facility, especially from ether mixed with a little alcohol, which deposits it in hard thick crystals an inch in length. It melts at  $76^\circ$ - $77^\circ$ , and solidifies with difficulty after fusion; cannot be distilled without decomposition. It is insoluble in water, and is gradually decomposed by boiling with it, emitting an unpleasant odour. Towards aqueous alkalis it is moderately stable at ordinary temperatures. Aqueous acids separate toluidine salt from it.

Toluidine fused with *chloral alcoholate* forms trichlorethylidene-ditolylamine,

which, when boiled with alcohol, appears to be converted into trichlorethylidene-oxethyltolylamine (Wallach).

**TOLYL CARBAMIC ETHERS** or **TOLYLURETHANES**. *Ethyltolylcarbamate*,  $\text{CO} \begin{Bmatrix} \text{NH}(\text{C}^2\text{H}^5) \\ \text{OC}^2\text{H}_5 \end{Bmatrix}$ , is obtained by the action of chlorocarbonic ether on toluidine in presence of ether. It crystallises with difficulty from the crude product in long prisms insoluble in water, easily soluble in alcohol and ether, melting at  $52^\circ$ . By distillation with phosphoric anhydride it yields tolyl isocyanate (Hofmann, *Proc. Roy. Soc.* xix. 108).

*Butyltolylcarbamate*,  $\text{CO} \begin{Bmatrix} \text{NH}(\text{C}^4\text{H}_9) \\ \text{OC}^4\text{H}_9 \end{Bmatrix}$ , is obtained by the action of butyl chlorocarbonate on liquid toluidine (b. p.  $198^\circ$ ). It is liquid, does not solidify at  $-10^\circ$ , and boils with partial decomposition at  $275^\circ$ – $280^\circ$ .

**TOLYLENEDIAMINES**,  $\text{C}^6\text{H}_4(\text{NH}_2)^2$  (Beilstein u. Kuhlberg, *Ann. Ch. Pharm.* clviii. 335; *Zeitschr. f. Chem.* [2], vii. 134). Three of these isomeric bases have been obtained, viz:

	1	2	3	4	5	6
1. Paraorthotolylene-diamine	$\text{C}^6\text{H}_4\text{NH}_2$	$\text{H}$	$\text{NH}_2$	$\text{H}$	$\text{H}$	$\text{H}$
2. Parametotolylene-diamine	$\text{C}^6\text{H}_4$	$\text{H}$	$\text{NH}_2$	$\text{NH}_2$	$\text{H}$	$\text{H}$
3. Metaorthotolylene-diamine	$\text{C}^6\text{H}_4$	$\text{NH}_2$	$\text{NH}_2$	$\text{H}$	$\text{H}$	$\text{H}$

1. *Paraortho*,  $\text{C}^6\text{H}_4(\text{NH}_2)^2$ — $\text{CH}_3$ .—This is the known form obtained by reduction of dinitrotoluene. Hofmann gives  $99^\circ$  as its melting point, and about  $280^\circ$  as the boiling point. The *sulphate*,  $\text{C}^6\text{H}_4(\text{NH}_2)^2\text{H}^2\text{SO}_4 + 2\text{aq.}$ , crystallises from water in long, prismatic, glistening crystals, which do not lose their water of crystallisation over sulphuric acid; 100 pts. of water at  $19.5^\circ$  dissolve 5.58 pts. of salt.

2. *Parametotolylene-diamine*,  $\text{C}^6\text{H}_4(\text{NH}_2)^2$ — $\text{CH}_3$ .—This modification is obtained by reduction of nitroparatoluidine with tin and hydrochloric acid. The solution is freed from tin by hydrogen sulphide, and evaporated to dryness; the residue, intimately mixed with pulverised caustic lime, is then distilled from a combustion-tube. It is obtained in brilliant white scales, which melt at  $88.5^\circ$ , and distil unchanged at  $265^\circ$ . It is moderately soluble in cold, more soluble in hot water. The aqueous solution of the base is extremely unstable, becoming black on standing for a few hours. The hydrochloride crystallises in long needles, extremely soluble in water. The *sulphate*,  $\text{C}^6\text{H}_4(\text{NH}_2)^2\text{H}^2\text{SO}_4 + 1\frac{1}{2}\text{H}_2\text{O}$ , forms magnificent, white, glistening scales; 100 pts. of water at  $19.5^\circ$  dissolve 9.29 pts. of salt. Both the free base and its salts become oxidised when exposed to the air, much more readily than paraorthotolylene-diamine and its salts.

3. *Metaorthotolylene-diamine*,  $\text{C}^6\text{H}_4(\text{NH}_2)^2$ — $\text{CH}_3$ . Nitro-orthotoluidine is attacked with great energy by tin and hydrochloric acid. The free base is colourless and crystalline; it melts at  $80^\circ$ , and boils constantly and unchanged at  $270^\circ$ . It is even less stable when exposed to the air than parametotolylene-diamine. The *sulphate*,  $\text{C}^6\text{H}_4(\text{NH}_2)^2\text{H}^2\text{SO}_4$ , is anhydrous and pulverulent, difficultly soluble in cold, more so in hot water. 100 pts. of water at  $11.5^\circ$  dissolve .84 pt. of the salt.

The following is a tabular arrangement of the characteristics of the isomeric tolylenediamines:

	Paraortho	Parameta	Metaortho
Melting point . . .	$90^\circ$	$88.5^\circ$	$80^\circ$
Boiling point . . .	$280^\circ$	$265^\circ$	$270^\circ$
The forms . . .	long prisms	scales	powder
$\text{H}^2\text{SO}_4$ contains . . .	$2\text{H}_2\text{O}$	$1\frac{1}{2}\text{H}_2\text{O}$	—
salt } 100 pts. $\text{H}_2\text{O}$ } dissolve }	5.58 pts. at $19.5^\circ$	9.29 pts. at $19.5^\circ$	0.84 pt. at $11.5^\circ$

**TOLYLURETHANES**. See TOLYL CARBAMIC ETHERS.

**TOLYLXYLIDINE**. See XYLIDINE.

**TOPAZ**. On the crystalline form of this mineral, see P. Groth (*Jahrb. f. Mineralogie*, 1870, 624; *Jahresb. f. Chem.* 1870, 1310). On its Pyroelectric properties, W. Hankel (*Jahrb. f. Mineralogie*, 1871, 287; *Chem. Soc. J.* [2], ix. 869). On the crystallographic and chemical relations of Topaz, Andalusite, and Staurolite, O. Rammeisberg (*Zeitschr. Geol. Ges.* xlv. 87).

**TOURMALINE.** A very fine black tourmaline from the granite of Giglio was found to have a specific gravity 3.15 and the following composition:

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	FeO	CaO	MgO	Na <sup>2</sup> O	K <sup>2</sup> O	B <sup>2</sup> O <sup>3</sup>	F
36.71	31.57	9.30	8.51	0.64	0.40	2.83	0.70	5.56	1.85 = 98.16.

This tourmaline is remarkable for its large percentage of ferrous oxide (E. Bechi, *Jahrb. f. Mineralogie*, 1872, 95).

**TRACHYTE.** For analyses of the trachytes of Lake Lanch, see L. Drossel (*Jahrb. f. Mineralogie*, 1870, 559; *Jahresb. f. Chem.* 1870, 1360); of the trachytes of Auvergne, see A. v. Lasaulx (*Jahrb. f. Mineralogie*, 1871, 673; 1872, 171, 281, 337; *Jahresb. f. Chem.* 1871, 1210; 1872, 1163).

**TRANSPIRATION OF LIQUIDS.** See LIQUIDS (p. 756).

**TRAP.** Vanadium and titanium have been found by Engelbach in the trap-rocks of the Rhine district, and by R. Apjohn in those of the Giant's Causeway, and in one from the Vicentine territory in Italy (*Chem. News*, xxvi. 183; *Chem. Soc. J.* [2], x. 1116).

**TRIACETAMIDE**,  $N(COCH^3)^2$ . See ACETAMIDE (p. 3).

**TRIACETYL-DERIVATIVES OF CARBO-HYDRATES.** See CELLULOSE (1st Suppl. 418); and the articles GLYCOGEN, INULIN, STARCH, and SUGAR, in this volume.

**TRIAMINES, CHROMIC.** See CHROMIUM (p. 336).

**TRIETHYLMELAMINE**,  $C^3H^7(C^2H^5)^3N^2$ , is formed, like triethylmelamine (1st Suppl. 808), by desulphuration of amyl-sulphocarbamide. It is a strongly alkaline syrup, insoluble in water and in hydrochloric acid. The *platinochloride*,  $C^3H^7(C^2H^5)^3N^2 \cdot 2HCl \cdot PtCl_4$ , forms a network of yellow crystals soluble in water, slightly soluble in alcohol. By boiling with hydrochloric acid it is decomposed, with evolution of ammonia (Hofmann, *Deut. Chem. Ges. Ber.* iii. 264).

**TRIBENZYHYDROXYLAMINE**,  $N(C^6H^5O)^2$ . See p. 155.

**TRIBENZYLAMINE.** See BENZYLAMINE (p. 182).

**TRIBROMHYDRIN.** See BROMHYDRINS (p. 209).

**TRIBROMO-DIOXYBENZOIC ACID**,  $C^6H^2Br^3O^4$ . See DIOXYBENZOIC ACID (p. 433).

**TRIBROMO-RESORQUINONE**,  $C^6HBr^3O^2$ . See RESORCIN (p. 1042).

**TRIBUTYLAMINE.** See BUTYLAMINES (p. 222).

**TRICHLORACETAMIDE.**

**TRICHLORACETIC ACID.**

**TRICHLORACETOLUIDE.**

} See ACETIC ACID (pp. 9, 10).

**TRICHLORACETOLACTIC ACID**,  $CCl^3-CH=CH-CH \begin{Bmatrix} OH \\ CO^2H \end{Bmatrix}$ . An acid produced by the prolonged action of strong hydrochloric acid on the corresponding cyanhydrin formed by the action of hydrocyanic acid on crotonic chloral. It melts at 40° (p. 400).

**TRICHLORETHYL OXIDE**,  $C^2H^3Cl^3O$ . See ETHYL OXIDE (p. 484).

**TRICHLORETHYLENE-DITOLYLAMINE**,  $CCl^3-CH[NH(C^7H^7)]^2$ . See TOLYLAMINES (p. 1179).

**TRICHLORHYDRIN.** See CHLORHYDRINS (p. 319).

**TRICHLOROCROTONAMIDE.**

**TRICHLOROCROTONIC ACID.**

} See CROTONIC ACID (pp. 397, 398).

**TRICHLOROFORMENE-SULPHOCHLORIDE.** On the reaction of this compound with potassium sulphite, see SULPHITES (p. 1136).

**TRICHLORO-DIBROMONITROETHANE**,  $C^2Cl^2Br^2(NO^2)^2$ , and **TRICHLOROTRINITROETHANE**,  $C^2Cl^3(NO^2)^3$ . See CARBON CHLORIDES (p. 259).

**TRICODINE**,  $C^{12}H^{12}N^4O^4$ . See CODINE (pp. 373-375).

**TRIDYMITE.** This variety of crystallised silica (1st Suppl. 1110) occurs but rarely in the older rocks, or in the newer rocks of a comparatively basic character; it is found chiefly in trachytes, associated with sanidin and acid plagioclases. It often occurs with hornblende, rarely with augite, never (like quartz) with olivin (F. Zirkol, *Pogg. Ann.* cxl. 492).

A. Streng has found tridymite in the porphyrites of Waldböckelheim, in very numerous small crystals, exhibiting the forms  $\infty P$  and  $oP$ , as well as the characteristic twin formations, and sometimes covered with octohedrons of magnetic oxide. With regard to this first observed occurrence of tridymite in the older rocks, Streng observes that the rock in which it occurs is not very acid, also that the amount of silica in the volcanic rocks which contain tridymite does not exceed 69 p. c. (*Jahrb. f. Min.* 1871, 933; 1872, 265; *Chem. Soc. J.* [2], ix, 128).

Tridymite has been found by Sandberger in small druses of a coarse-grained dolerite of the Frauenberg, near Heubach; by H. Wolf in the trachyte from the neighbourhood of Quito; by G. vom Rath very abundantly in the porous scoraceous trachytes of the Stenzelberg in the Siebengebirge, also in outcasts from Vesuvius in the eruption of 1822; by K. Hofmann in the pores of the augitic andesites of the Guttin and Royals ranges (*Jahresb. f. Chem.* 1872, 1098).

**TRIEPIO ACID.** An acid said by Maumené (*Compt. rend.* lxxv. 85) to be formed by the action of potassium permanganate on cane-sugar.

**TRIETHIDE, STANNIC.** See STANNETHYLS and TIN (p. 1159).

**TRIETHYLARSINE.** See ARSINES (p. 107).

**TRIETHYL-CARBINOL**,  $C^3H^{10}O = (C^2H^5)^3.COH$ . This tertiary heptyl alcohol is formed by the action of zinc-ethyl (2 mols.) on propionyl chloride (1 mol.) The mixture after a few hours forms a thick mass, and on decomposing this mass with water and distilling, the alcohol passes over, together with an oily body which remains undissolved when the whole is treated with a large quantity of water. The alcohol is separated from the aqueous solution by means of potassium carbonate, then dried with baryta and rectified.

Triethyl-carbinol is a colourless liquid having a sp. gr. of 0.8593 at  $0^\circ$ , becoming viscid at  $-20^\circ$ , and boiling at  $140^\circ$ – $142^\circ$ . It has a camphorous odour, and an aromatic taste, burning at first, but afterwards cooling. By oxidation with chromic acid mixture it yields a hydrocarbon which unites with bromine, and probably consists of heptylene,  $C^7H^{14} = C \left\{ \begin{smallmatrix} (C^2H^5)^2 \\ CH.CH^2 \end{smallmatrix} \right.$ . Acetic acid was also formed, together with a more highly carbonated acid (propionic acid). Diethylketone does not appear to be formed (Nabapetian, *Zeitschr. f. Chem.* [2], vii. 274).

**TRIETHYL-METHANE**,  $CH(C^2H^5)^3$ . A modification of heptane, produced by the action of zinc-ethyl and sodium on orthoformic ether. The crude product is fractionated, the portion distilling at about  $100^\circ$  is agitated with sulphuric acid, and the undissolved portion is washed, dried, and rectified. Triethylmethane thus obtained is a colourless liquid having a faint odour of petroleum, a sp. gr. of 0.689 at  $27^\circ$ , and boiling at  $96^\circ$ . Vapour-density = 101.5° (Ladenburg, *Deut. Chem. Ges. Ber.* v. 762).

**TRIETHYL-PHOSPHINE OXIDE.** See PHOSPHINES (p. 953).

**TRIETHYL-PYROPHOSPHOSULPHOBROMIDE**,  $P^2S^3(OC^2H^5)^3Br$ . See SULPHOPHOSPHORIC ETHERS (p. 1123).

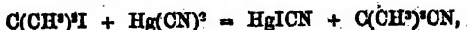
**TRIETHYL-SILICOL.** See SILICIC ETHERS (p. 1083).

**TRIETHYLSULPHINE PERIODIDE.** See IODIDES (p. 678).

**TRIGENIC ACID.** The trigenic acid of the allyl series,  $C^3H^5N^3O^3$ , is formed by the action of cyanic acid on acrolein (p. 26).

**TRIGLYCOLLAMIC ACID.** On the constitution of this acid, see Heints (*J. pr. Chem.* [2], iii. 69, 120; *Chem. Soc. J.* [2], ix, 236) and Claus (*J. pr. Chem.* [2], iii. 123).

**TRIMETHACETIC ACID**,  $C^3H^5O^3 = C(CH^3)^3.CO^2H$  (Butlerow, *Deut. Chem. Ges. Ber.* v. 478). This acid is best prepared by acting on tertiary butyl iodide,  $C(CH^3)^3I$ , with mercuric cyanide, whereby tertiary butyl cyanide is produced:



digesting this cyanide with alcoholic potash, and decomposing the resulting potassium salt with sulphuric acid. By dehydrating the distillate with phosphoric anhydride, trimethacetic acid is obtained as a vitreous mass intersected by crystals. It melts at  $34^\circ$ – $36^\circ$ , and boils at  $161^\circ$ ; is not deliquescent, but dissolves slowly in water. The barium salt,  $(C^3H^5O^2)^2Ba + 5H^2O$ , is easily soluble, and crystallises in stellate needles. The silver salt,  $C^3H^5O^2Ag$ , crystallises from aqueous solution in laminae, from an acid solution in small needles, a reaction by which it is distinguished from the silver salt of ordinary valeric acid.

**TRIMETHYL-CARBINOL**,  $C(CH_3)_3COH$ . See BUTYL ALCOHOLS (p. 219).

**TRIMETHYLENE GLYCOL** and **ETHERS**. The bromide,  $C_3H_6Br_2$ , is formed by the action of hydrobromic acid on allyl bromide (p. 40). See PROPYLENE-COMPOUNDS (pp. 1017, 1020).

**TRIMETHYL-ETHYL-METHANE**,  $C_8H_{18} = C \begin{Bmatrix} (CH_3)_3 \\ C_2H_5 \end{Bmatrix}$ . This form of hexane, produced by the action of zinc-ethyl on tertiary butyl iodide, is a colourless liquid boiling between  $43^\circ$  and  $48^\circ$ , and having a vapour-density = 2.917.

**TRIMETHYL-PHENYLAMMONIUM IODIDE**,  $(CH_3)_3(C^6H_5)N.I$ . On the formation of dimethyltoluidines by the action of heat on this compound, see AMINES (p. 57).

**TRIMETHYL-TOLYLAMMONIUM IODIDE**,  $(CH_3)_3(C^6H_4)N.I$  (p. 58).

**TRINITRO-AZO-BENZENE**. When crystals of azobenzene are dissolved in nitric acid of sp. gr. 1.5, and the solution is boiled, sulphur-yellow crystals of trinitro-azoxybenzene,  $C_6H_3(NO_2)_3NO$ , gradually separate out, and afterwards needles of trinitro-azobenzene,  $C_6H_3(NO_2)_3N$ , which melt at  $112^\circ$  (Petrie, *Zeitschr. f. Chem.* [2], vi. 564).

**TRINITRO-CRESOTIC ACID**,  $C_8H_3(NO_2)_3O_2$ . This is the composition of *nitrococcus acid*, the product of the action of nitric acid on carminic acid. See COCHINEAL (p. 367).

**TRINKERITE**. A fossil resin occurring in the Eocene lignite of Carpano, near Albano in Istria, in thick transparent and translucent masses, having a fatty lustre and hyacinth-red to chestnut-brown colour. It has a flat conchoidal fracture, and is often traversed by parallel clefts. Hardness = 1.5 to 2; sp. gr. = 1.025. Becomes strongly electric when rubbed. Melting point  $168^\circ$ – $180^\circ$ . When heated it gives off pungent vapours rich in hydrogen sulphide. It is insoluble in water, sparingly soluble in ether and in alcohol, perfectly soluble in hot benzene. An analysis by H. Hlasiwetz gave, without any ash, the numbers *a* (Tschermak, *J. pr. Chem.* [2], ii. 258).

Trinkerite has also been found by Niedzwiedzki (*Jahrb. f. Mineralogie*, 1871, 641) in flat lumps imbedded in a carbonaceous marl at Gams, near Hieflau in Styria. An analysis, also by Hlasiwetz, gave the numbers *b*.

	O	H	O	S
<i>a.</i>	81.1	11.2	3.0	4.7 = 100
<i>b.</i>	81.0	10.0	3.1	4.1 = 100

The composition does not differ much from that of Tasmanite (v. 698) (Tschermak, *J. pr. Chem.* [2], ii. 258).

A resin, intermediate between retinite and trinkerite, occurring in the lignite of Agka, in the Bakonyer forest, Veszprémer Comitat, Hungary, consists, according to Hlasiwetz, of 81.69 C., 10.20 H., 1.87 S., and 6.34 O. (= 100).

**TRIOXYADIPIC ACID**,  $C_8H_4O_7$ . See ADIPIC ACID (p. 29).

**TRIOXYTERMIC**, **TRIOXYCHLORIC**, and **TRIOXYIODIC ACIDS**. These names are given by Kämmerer to BROMIC, CHLORIC, and IODIC ACIDS (p. 592).

**TRIOXYNAPHTHALENE**,  $C_{10}H_4O_3$ . See NAPHTHOLS (pp. 841, 842).

**TRIOXYNAPHTHAQUINONE**,  $C_{10}H_2O_3$ . See NAPHTHAQUINONE (p. 837).

**TRIPHENYLAMINE**,  $N(C^6H_5)_3$ . See PHENYLAMINES (p. 945).

**TRIPHENYL-BIURET**,  $C_{18}H_{15}N_3O_2$ . See BIURET (p. 193).

**TRIPHENYL-METHANE**,  $CH(C^6H_5)_3$ . See PHENYLMETHANES (p. 948).

**TRIPHENYLBISANILINE-SULPHONIC ACID**. See ANILINE (p. 77).

**TRISALICENO-SALICENIN**,  $C_{15}H_{10}O_8 = 4C^6H_5O_2 - 3H_2O$ . See SALICENIN (p. 857).

**TRISALICYLO-SALICYLIC ACID**. See SALICYLIC ANHYDRIDES (p. 1067).

**TRISULPHOXYALATES**. See SULPHAZOTISED ACIDS (p. 1111).

**TRITHIONIC ACID**. See SULPHUR, OXYGEN ACIDS OF (p. 1141).

**TRITICUM**. On the constituents of the rhizomes of *Triticum repens*, see Ludwig a. Müller (*Arch. Pharm.* [2], cl. 132; *Chem. Soc. J.* [2], x. 840).

**TRÖGGERITE**. See URANIO ARSENATES (p. 1190).

**TRONA**. O. Popp (*Ann. Ch. Pharm.* clv. 348) has analysed three sorts of Egyptian Trona: *a*, small transparent prismatic crystals, having nearly the com-

position,  $2\text{Na}^+\text{O}\cdot3\text{CO}^+ + 4\text{H}^+\text{O}$ ;  $b$  and  $c$  very impure saline masses, with few or no distinct crystals:

$2\text{Na}^+\text{O}\cdot3\text{CO}^+$	$\text{Na}^+\text{O}\cdot\text{SO}^+$	$\text{NaCl}$	$\text{CaO}\cdot\text{SO}^+$	$\text{H}^+\text{O}$	Insol.
64.3	1.5	8.4	1.3	22.5	1.65 = 90.65
32.2	24	33.3	—	8.87	1.35 = 99.72
26.15	66.66	2.63	—	4.05	0.40 = 99.80

See, further, CARBONATES (p. 268).

**TUFA.** On the composition of the tufas of Ichia, see C. W. Fuchs (*Jahrb. f. Mineralogie*, 1873, 429; *Jahresb. f. Chem.* 1872, 1168).

**TUNGSTEN.** Atomic Weight, 184.—Very exact experiments on this metal and its compounds have lately been made by Roscoe (*Proceedings of the Lit. and Phil. Soc. of Manchester*, January 23, 1872; *abst. Chem. Soc. J.* [2], x. 286).

**Metallic Tungsten.**—Tungstic oxide was prepared by decomposing commercial crystallised sodium tungstate with hydrochloric acid, dissolving the washed precipitate in ammonia, and igniting the recrystallised ammonium salt in an open crucible. Tungstic oxide thus obtained is a heavy powder, having a canary-yellow colour at ordinary temperatures, but acquiring a dark orange-colour when heated. The smallest admixture of sodium salt gives it a greenish colour; the same tint is also imparted to it by the action of light, which occasions a partial reduction. The pure metal obtained by heating this oxide to bright redness in a platinum or porcelain tube through which a stream of hydrogen is passed, is a granular powder having a light grey colour and strong lustre. By oxidation, it increases in weight by 26.01 p.c.; the atomic weight, 184, requires an increase of 26.09 p.c.

To obtain exact determinations of the atomic weight, the trioxide prepared from the oxychloride, to be presently described, was ignited in a platinum dish and then reduced by heating it in a stream of hydrogen. The atomic weight thence deduced was 183.84. Secondly, the hexchloride,  $\text{WCl}_6$ , was heated in a stream of hydrogen, the resulting hydrochloric acid was determined, and the residual metallic tungsten weighed. This experiment gave  $W = 184.25$ , the mean of which and the preceding number is 184.04.

**Chlorides.** The hexchloride,  $\text{WCl}_6$ , is formed by the action of chlorine on metallic tungsten, at a moderate heat, the combination being attended with ignition. The chlorine must be perfectly dry and free from oxygen, otherwise oxychloride will be formed at the same time, which it is not possible to separate from the chloride. The pure hexchloride forms a black-violet, crystalline sublimate, which, when considerable quantities are distilled, condenses in dark-red drops. The solidified mass decrepitates when cold; when pure, it does not alter in contact with moist air, but if the slightest trace of oxychloride is present, it absorbs moisture and decomposes. Water does not act on the pure chloride at temperatures below  $60^\circ$ , but the impure chloride is immediately decomposed by water even in the cold, into hydrochloric acid and yellow (or greenish-yellow) oxide. The chloride dissolves very easily in carbon sulphide, and separates out on cooling or evaporation of the dark red-brown solution, in brown hexagonal crystals. It melts at  $276^\circ$  (corr.), but the smallest contamination with oxychloride lowers the melting point by nearly  $100^\circ$ . It solidifies at  $270^\circ$  and under a pressure of 759 mm., boils constantly at  $346.7^\circ$ . The vapour-density, determined in sulphur-vapour ( $440^\circ$ ) was = 168.8; ( $H = 1$ ) in mercury-vapour ( $350^\circ$ ) = 190.9. The calculated value is 198.6. Hence, it appears that dissociation takes place between  $350^\circ$  and  $440^\circ$ , and, in fact, direct experiments indicated a resolution of the hexchloride into pentachloride and free chlorine. This may explain the result obtained by Deville, who found the vapour-density to be 164.3 (at  $350^\circ$ ), which was regarded as supporting the view suggested by Persoz, that tungsten is a pentad element with the atomic weight  $Tu = 153.3$ , its highest chloride being accordingly represented by the formula  $\text{TuCl}_5$  (v. 899).

**Pentachloride,  $\text{WCl}_5$ .**—This compound was prepared by partially reducing the hexchloride at a low temperature in a current of hydrogen, and then distilling off the volatile pentachloride from the non-volatile tungsten-compounds containing (less chlorine, formed at the same time. It crystallises in black, shining, highly deliquescent needles, which melt at  $248^\circ$  and boil at  $275.6^\circ$ . Vapour-density, obs. = 182.8 (in mercury-vapour); calc. = 180.7.

**Tetrachloride and Dichloride.**—The tetrachloride,  $\text{WCl}_4$ , forms the non-volatile residue produced in the distillation of the hexchloride in hydrogen, provided that the temperature has not been allowed to rise too high. It is a soft, crystalline, highly hygroscopic powder, of a greyish-brown colour; it decomposes, when strongly heated, into the volatile pentachloride and dichloride which remains behind. The dichloride,  $\text{WCl}_2$ , is a loose grey powder, without lustre or crystalline structure. It



is not permanent in the air, is dissolved in small quantity by water, but the greater part is decomposed into brown oxide ( $\text{WO}^2$ ), and hydrochloric acid. It reduces nitric acid, forming ammonium nitrate:



**Oxychlorides.**—The *monooxychloride*,  $\text{WCl}^3$ , is obtained by passing the vapour of the penta- or hex-chloride over the heated oxide or dioxychloride in a current of chlorine. It occurs in beautiful ruby-red crystals, which melt at  $210.4^\circ$ , and volatilise at  $227.5^\circ$ , and on exposure to air become at once coated with a yellow crust of the dioxychloride. Vapour-density in sulphur-vapour =  $171.5^\circ$ ; in mercury-vapour =  $173^\circ$ ; calc. = 171.

The *dioxychloride*,  $\text{WO}^2\text{Cl}^2$ , is best obtained by the action of chlorine on the brown dioxide. It sublimes at a moderate heat, without previous fusion, in light yellow, shining, four-sided laminae, partly decomposing however into trioxide and monooxychloride.

**Bromides.** By the action of excess of bromine on tungsten, a *penta-* and not a *hexbromide* is obtained. The crystals of the pentabromide,  $\text{WBr}^5$ , have a dark metallic lustre, resembling iodine; they undergo a slight decomposition by keeping, bromine being liberated. When the pentabromide is heated to  $350^\circ$  in a current of hydrogen, the *tribromide*,  $\text{WBr}^3$ , is produced. Some slight indication of the formation of the compound  $\text{WBr}^4$  was also observed, but it was not isolated.

**Oxybromides.**—The oxybromides,  $\text{WOBr}^4$  and  $\text{WO}^2\text{Br}^2$ , closely resemble the oxychlorides, and are prepared in a similar manner.

**Iodide**,  $\text{WI}^3$ . Tungsten appears to form but one compound with iodine, the *diiodide*, which is produced when iodine vapour is passed over heated metallic tungsten, or over the brown oxide. It is a somewhat unstable compound, losing its iodine when heated in the air, and becoming converted into tungstic acid.

**TURMERIC.** On the colouring matter of turmeric, see CURCUMIN (p. 403).

**TURPENTINE OIL.** On the action of phosphonium iodide on turpentine oil, see HYDROCARBONS (p. 657).

On the formation of Cymene from turpentine oil, see CYMENE (p. 419).

The converse reaction does not appear to have been effected. According to Louguine (*Deut. Chem. Ges. Ber.* v. 730), cymene is not converted into turpentine oil, either by the action of sodium-amalgam on a solution of turpentine oil in aqueous alcohol mixed with a little ether, or by adding sodium to its alcoholic solution.

On the chemical relation of *phosphorus* to turpentine oil, and the action of the latter as an antidote in phosphorus poisoning, see Köhler a. Schimpf (*Chem. Centr.* 1872, 294; *Jahresh. f. Chem.* 1872, 242; *Chem. Soc. J.* [2], xi. 179).

**TUTU.** See CORIARIA (p. 391).

**TYRITE.** This mineral, from Helle near Arendal, has been analysed by Rammelsberg (*Deut. Chem. Ges. Ber.* iii. 926).

$\text{Nb}^2\text{O}^5$	$\text{SnO}^2$	YO	CeO	$\text{LaO DIO}$	FeO	$\text{UO}^2$	CaO	$\text{H}^2\text{O}$
45.00	1.05	30.0	5.74	3.51	1.48	6.52	2.46	4.88 = 100.54.

See also TANTALATES (p. 1146).

**TYROSINE.** According to Béchamp (*Compt. rend.* lxxiv. 115, 184), this substance is formed, together with leucine, in alcoholic fermentation induced by beer-yeast.

## U

**ULLMANNITE.** *Antimonial and Arsenical Nickel-glance* (iv. 43).—Hemihedral crystals of this mineral from Lölling in Carinthia have been examined by Zepharovich (*Wien. Akad. Ber.* [1 Abth.], lx. 809). They exhibit the faces  $\pm \frac{0}{2}$ ,  $\infty\text{O}$ ,  $\pm \frac{202}{2}$ ,

$\frac{20}{2}$  and  $\frac{80}{2}$ . Sp. gr. = 6.54–6.74. An analysis by W. Gintl gave the values A. which when corrected for admixed metallic bismuth and galena gave those in B. The  
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# 1186 ULTRAMARINE—URAMIDOBENZOIC ACID.

formula  $\text{NiS.Ni}(\text{Sb}; \text{As})$ , supposing  $\frac{1}{10}$  of the antimony to be replaced by arsenic, requires the values O:

	S	Sb	As	Ni	Bi Pb	
A.	15.22	50.53	3.10	27.38	3.80	= 100.12
B.	15.73	52.56	3.23	28.48	—	= 100
C.	15.36	52.71	3.60	28.32	—	= 100

Tin-white to steel-grey ullmannite from the micaceous clay slate of the Rinkeberg in Carinthia exhibits the faces  $\infty\text{O}\infty$ ,  $\infty\text{O}$ , and cleaves parallel to the cubic faces. Sp. gr. = 6.63. Its analysis gave

S	Sb	As	Ni*	
15.28	56.07	6.94	27.50	= 99.79.

\* With traces of cobalt.

(M. v. Lill, *Jahrb. f. Min.* 1871, 641).

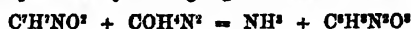
Ullmannite free from arsenic occurs, with spathic iron ore, in clefts of the limestone near Waldstein, in Carinthia, usually in laminar or granular aggregates, rarely in crystals. The crystals exhibit the combination  $\infty\text{O}\infty$ .  $\text{O}\infty\text{O}$ , without any indication of hemihedral forms. Decomposition and mutual action of the mineral and the ground-mass is indicated by the presence of a calcic antimonate,  $3\text{CaO}.2\text{Sb}^2\text{O}^3 + 6\text{H}^2\text{O}$ , which occurs on the vein, partly as a greenish earthy mass, partly in pseudomorphous crystals of the form above described (Rumpf u. Ullik, *Jahrb. f. Min.* 1870, 355).

**ULTRAMARINE.** On the composition of Ultramarine, see Fürstenau (*Dingl. pol. J.* cci. 176; *Jahresb. f. Chem.* 1871, 1019); Stein (*J. pr. Chem.* [2], iii. 39; *Chem. Soc. J.* [2], ix. 166; *Jahresb.* 1871, 1020). On the blue-burning of ultramarine direct from the raw mass: Fürstenau (*Dingl. cii.* 446; *Jahresb.* 1871, 1019). On the supposed incapability of Potash to form Ultramarine; Stein (*J. pr. Chem.* [2], iii. 137; *Chem. Soc. J.* [2], ix. 451).

**UMBELLIFERONE,  $\text{C}^8\text{H}^4\text{O}^2$ .** From experiments by Kachler, reported by Hlasiwetz (*Deut. Chem. Ges. Ber.* [2], ix. 550), it appears that umbelliferone, heated to  $100^\circ$  with acetyl chloride, is converted into monacetyl-umbelliferone,  $\text{C}^8\text{H}^4(\text{C}^2\text{H}^3\text{O})\text{O}^2$ , which, after recrystallisation from dilute alcohol, forms small colourless needles, nearly insoluble in water, easily soluble in warm alcohol, and fluorescent, though somewhat less strongly than pure umbelliferone.

Umbelliferone boiled with strong potash yields resorein, together with carbonic and formic acids. Hlasiwetz represents it by the formula  $\text{C}^8\text{H}^4(\text{CH}^3\text{O})^2(\text{CO}^2\text{H})$ .

**URAMIDOBENZOIC ACID,  $\text{C}^8\text{H}^4\text{N}^2\text{O}^3$ .** This acid, discovered by Griess (1st *Suppl.* 318), may be produced by melting together urea and amidobenzoic acid:



and its ethylic ether in like manner by fusing urea with ethylic amidobenzoate (see *BENZOIC ACID DERIVATIVES*, p. 166).

**Nitro-uramidobenzoic Acids** (Griess, *J. pr. Chem.* [2], v. 227; *Deut. Chem. Ges. Ber.* v. 192; *Proc. Roy. Soc.* xx. 168). The dinitro-uramidobenzoic acid,  $\text{C}^8\text{H}^2(\text{NO}^2)^2\text{O}^3$ , formed by the action of strong nitric acid on uramidobenzoic acid (1st *Suppl.* 318), is a mixture of three isomeric acids, which cannot be separated from each other, owing to the great similarity of their properties.

When the solution of the three dinitro-acids in aqueous ammonia is boiled for some time, they are converted into the mono-nitro-acids:



By adding barium chloride to the hot solution on cooling, the barium salt of the  $\beta$ -acid is separated in needle-shaped crystals. On concentrating the mother-liquor of this salt by evaporation, the salt of the  $\alpha$ -acid separates in microscopic needles; the barium salt of the third acid is obtained by boiling the mother-liquor from the previous salt to dryness, and washing the residue with water. It crystallises from hot water in bright yellow scales.

The three acids set free from the barium salts by means of hydrochloric acid have the following properties:

*$\alpha$ -Nitro-uramidobenzoic acid,  $\text{C}^8\text{H}^3(\text{NO}^2)\text{N}^2\text{O}^3$ ,* crystallises in bright yellow needles or small plates; it is very slightly soluble in cold water, sparingly in hot, and freely in hot alcohol.

*$\beta$ -Nitro-uramidobenzoic acid* crystallises in slender yellow needles, and is also much more freely soluble in alcohol than in water.

*γ-Nitro-uramidobenzoic acid* is very slightly soluble in all neutral solvents, and forms small yellow scales. When the free acid and its salts are boiled with water for a considerable time, the following decomposition takes place:



The  $\alpha$ - and  $\beta$ -acids are reduced by tin and hydrochloric acid to the amido-acids. *α-Amido-uramidobenzoic acid*,  $\text{C}^6\text{H}^4(\text{NH}^2)\text{N}^2\text{O}^3$ , is but slightly soluble in hot water, and less so in alcohol; it forms a white silver salt,  $\text{C}^6\text{H}^4\text{N}^2\text{O}^3\text{Ag}$ , and a hydrochloride,  $\text{C}^6\text{H}^4\text{N}^2\text{O}^3\cdot\text{HCl}$ , which is almost insoluble, even in very dilute hydrochloric acid. *β-Amido-uramidobenzoic acid* is very little soluble in water, and, curiously enough, does not combine with acids, but forms metallic salts having the formula  $\text{C}^6\text{H}^4\text{N}^2\text{O}^3\text{M}$ . On boiling this acid with hydrochloric acid or baryta-water, it gives off ammonia, and a new acid is formed, which may be regarded as amidobenzoic acid, in which one atom of hydrogen is replaced by  $(\text{CO})\text{N}$ , and may therefore be called *β-amidocarboxamidobenzoic acid*,  $\text{C}^6\text{H}^4(\text{NH}^2)(\text{CO}(\text{N}))\text{O}^2$ ; this acid forms white nodules insoluble in all neutral solvents.

*γ-Nitro-uramidobenzoic acid* is not reduced by the action of tin and hydrochloric acid, but undergoes the following decomposition:—



The new compound is *γ-amidocarboxamidobenzoic acid*. It forms white needles, which are almost insoluble in water, alcohol, and ether.

By the action of nitric acid, the mononitro-acids are again converted into the dinitro-acids, which can thus be obtained in the pure state. They closely resemble one another, forming yellowish white needles, which are readily soluble in alcohol and ether, but scarcely soluble in cold water. The barium-salts of the  $\alpha$ - and  $\beta$ -acids are very sparingly soluble; that of the former crystallises in microscopic needles, that of the latter is amorphous. Barium *γ*-dinitro-uramidobenzoate is somewhat more readily soluble, and forms long slender yellow needles.

The three dinitro-acids are converted into the corresponding nitro-amido-benzoic acids, when their aqueous solutions are boiled for a considerable time:



*α-Nitro-amidobenzoic acid*,  $\text{C}^6\text{H}^4(\text{NO}^2)(\text{NH}^2)\text{O}^2$ , is readily soluble in hot alcohol, but only sparingly soluble in water, and forms yellow prisms. The barium salt,  $(\text{C}^6\text{H}^3\text{N}^2\text{O}^3)^2\text{Ba} + 3\text{H}^2\text{O}$ , crystallises in yellowish-red needles, and is readily soluble in water.

*β-Nitro-amidobenzoic acid* crystallises from hot alcohol in clusters of glistening, yellowish-red needles, or small plates. When gently heated it sublimes in shining rhombic plates, without previous melting. Its barium salt,  $(\text{C}^6\text{H}^3\text{N}^2\text{O}^3)^2\text{Ba} + 2\text{H}^2\text{O}$ , is only slightly soluble in boiling water, and crystallises in bright, yellowish-red prisms.

*γ-Nitro-amidobenzoic acid* is very readily soluble in hot water and in cold alcohol and ether. It forms yellow prisms, which melt when heated to a brown oil, and decompose with slight explosion at a higher temperature. The barium salt,  $(\text{C}^6\text{H}^3\text{N}^2\text{O}^3)^2\text{Ba} + 7\text{H}^2\text{O}$ , is easily soluble, even in cold water.

On gently warming these three nitro-amido-acids with tin and hydrochloric acid, the corresponding diamido-acids are formed. *α-Diamidobenzoic acid*,  $\text{C}^6\text{H}^4(\text{NH}^2)^2\text{O}^2$ , is sparingly soluble in hot water, and crystallises in minute but well-defined short prisms. It is remarkable for the extremely sparing solubility of its sulphate,  $\text{C}^6\text{H}^4\text{N}^4\text{O}^4\cdot\text{SO}^4\text{H}^2$ .

The *β-diamido-acid* is rather readily soluble in hot water, and forms pale yellow plates. Its sulphate has the composition  $[\text{C}^6\text{H}^3(\text{NH}^2)^2\text{O}^3]^2\text{SO}^4\text{H}^2$ , and is a little more soluble than that of the  $\alpha$ -acid. The *γ-acid* crystallises in long, yellowish-white needles; the sulphate,  $(\text{C}^6\text{H}^3\text{N}^2\text{O}^3)^2\text{SO}^4\text{H}^2 + 1\frac{1}{2}\text{H}^2\text{O}$ , forms white, six-sided tables, and is almost as insoluble as that of the  $\alpha$ -acid.

When the  $\alpha$ -diamido-acid is dissolved in warm, dilute, hydrochloric acid, insufficient to dissolve the whole, and the filtered solution is mixed with sodium nitrite, an explosive compound, crystallising in long needles, is formed. This body has no acid properties, but combines readily with acids, forming well-crystallised salts. Its formula is probably  $\text{C}^6\text{H}^4\text{N}^4\text{O}^4$ . In presence of free hydrochloric acid, this basic compound is not formed, but nitrogen is evolved, and an amorphous reddish-brown acid is deposited.

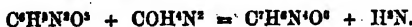
The hydrochlorides of the two other amido-acids behave differently with sodium nitrite; they both yield *azo-acids*. That from the  $\beta$ -compound is very sparingly soluble in water, and forms white, short needles, which, when heated in the dry state, melt and blacken; a small portion subliming, but the greater part being completely

decomposed. The barium salt,  $(C^6H^4N^2O^4)^2Ba + 4H^2O$ , is readily soluble in hot water, and crystallises in slender, colourless needles. The  $\gamma$ -*azo*-acid crystallises in long, hair-like, silky needles. It is more soluble than the  $\beta$ -acid; when gently heated it melts to a yellow oil, with partial sublimation; at a higher temperature it decomposes, with a slight explosion. The white needles of its barium salt,  $(C^6H^4N^2O^4)^2Ba + 2H^2O$ , are only sparingly soluble in hot water.

When either of the diamido-acids is submitted to dry distillation, it splits up into carbon dioxide and a phenylene-diamine. That from the  $\alpha$ -acid is identical with the diphenylamine which is obtained from the nitroaniline prepared from substituted anilides. The  $\beta$  and  $\gamma$ -acids yield one and the same phenylene-diamine, which, however, is not identical with that derived from dinitrobenzene, but is a new isomeric modification. It crystallises from hot water in white, rectangular, four-sided tables, melting at  $99^\circ$ , and boiling at about  $252^\circ$ . The *sulphate*,  $C^6H^4(NH^2)^2SO^4H^2 + 1\frac{1}{2}H^2O$ , crystallises in pearly scales. The *platinum salt* is precipitated in the form of brownish-red needles. When ferric chloride is added to a solution of the base in hydrochloric acid, ruby-red needles are formed, consisting of the hydrochloride of a new base, which probably has the composition  $C^{12}H^4N^4$ .

There is a fourth diamidobenzoic acid known, which Voit has obtained by reducing dinitrobenzoic acid. This body is distinguished from its isomerides, not only by its physical properties, but especially by not yielding a volatile base when submitted to distillation, being completely carbonised, with evolution of ammonia.

**URAMIDODINITROPHENYLIC ACID,**  $C^6H^4N^2O^4 = C^6H^4(CO^2H^2N^2)(NO^2)^2O$  (Grüss, *J. pr. Chem.* [2], v. 1). When picramic acid is added to an equal weight of melted urea, ammonia is evolved, and the whole soon solidifies to a brown mass; and on dissolving this mass in dilute ammonia, and adding hydrochloric acid to the solution, uramidodinitrophenylic acid is precipitated, and may be purified by repeated crystallisation from boiling water. Its formation is thus represented:—



Uramidodinitrophenylic acid dissolves with difficulty in boiling water, and crystallises out on cooling in long narrow plates of a bright yellow colour. It is readily soluble in hot alcohol, and yields crystalline salts with bases. Its barium salt forms blood-red needles, and its silver salt,  $C^6H^4N^2O^4.Ag$ , is a reddish-yellow amorphous precipitate.

*Amido-uramidodinitrophenylic acid*,  $C^6H^4N^2O^4 = C^6H^4(NH^2)\left[\begin{smallmatrix} CO \\ H^2 \end{smallmatrix}\right]N^2(NO^2)^2O$ , is prepared from the acid just described by treating it with ammonium sulphide. The blood-red solution is carefully decomposed by hydrochloric acid, and the precipitate treated with hot water. After separation of the sulphur by filtration, the solution is first rendered alkaline by ammonia, and then acidified with acetic acid. The acid thus obtained crystallises in reddish-brown needles, which are soluble with difficulty both in hot water and alcohol, and scarcely soluble in ether. It forms compounds both with acids and bases, the latter being very stable. The *hydrochloride*,  $C^6H^4N^2O^4.HCl$ , is precipitated in white glistening scales on adding concentrated hydrochloric acid to a solution of the new acid in warm dilute hydrochloric acid. It is readily soluble in pure water. On mixing a hot concentrated ammoniacal solution of amido-uramidodinitrophenylic acid with barium chloride, the *barium compound*,  $(C^6H^4N^2O^4)^2Ba + 3\frac{1}{2}H^2O$ , is precipitated in steel-blue glistening needles, which dissolve freely in hot, sparingly in cold water.

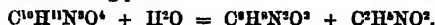
*Amidocarboxamidodinitrophenylic acid*,  $C^6H^4N^2O^4 = C^6H^4(NH^2)[(CO)N](NO^2)^2O$ .—On boiling the hydrochloric acid solution of amido-uramidodinitrophenylic acid for a quarter of an hour, ammonia is eliminated, and solidifies on cooling to a pulp of crystals, consisting of amido-carboxamidodinitrophenylic acid. This acid dissolves with difficulty in boiling water, and crystallises therefrom in golden-yellow needles. It is much more soluble in alcohol than in water, but only slightly soluble in ether. Like the preceding it combines both with acids and with bases, but the former compounds are very unstable. The *hydrochloride*,  $C^6H^4N^2O^4.HCl + H^2O$ , formed by dissolving the acid in hot moderately concentrated hydrochloric acid, crystallises in white glistening plates, which at  $100^\circ$  lose both their water and hydrochloric acid, leaving pure amidocarboxamidodinitrophenylic acid. The *barium salt*,  $(C^6H^4N^2O^4)^2Ba$ , forms yellow difficultly soluble needles.

*Diamidocarboxamidodinitrophenylic acid*,  $C^6H^4N^2O^4 = C^6H^4(NH^2)[(CO)N]O$ .—Amidocarboxamidodinitrophenylic acid, when treated with tin and hydrochloric acid, yields a very difficultly soluble stannochloride of the diamidated acid. On decomposing this salt with sulphuretted hydrogen, the hydrochloride  $C^6H^4N^2O^4.HCl$  is obtained in white plates, which become brown when exposed to the air in the moist state. The

free acid, prepared from this compound by the addition of ammonia to its solution in boiling water, forms needles which are difficult to obtain colourless, as they oxidise and become brown on exposure to the air. This acid is but very slightly soluble in boiling water, and still less so in alcohol or ether. It combines with mineral acids, forming monacid compounds, and dissolves in potash-solution and baryta-water, but is reprecipitated by carbonic acid.

**URAMIDODRACYLIC ACID**,  $C^6H^3N^2O^4$ , is formed in urea and para-amidobenzoic acid in the same manner as uramidobenzoic acid from urea and amidobenzoic acid (p. 166).

**URAMIDOHIPPURIC ACID**,  $C^{10}H^{11}N^2O^4$ , is the chief product obtained by fusing urea with amidohippuric acid. It is very soluble in hot water, and crystallises therefrom in nodules. Its *silver salt*,  $C^{10}H^{10}N^2O^4Ag$ , is a white crystalline precipitate. By prolonged boiling with strong hydrochloric acid, uramidohippuric acid is resolved into uramidobenzoic acid and glycerin:



When heated by itself it does not yield carboxamidohippuric acid, nevertheless this acid is formed in small quantity in the preparation of uramidohippuric acid. It is very slightly soluble in water, and crystallises therefrom in narrow shining laminae or six-sided tablets. Its *barium salt*,  $C^{10}H^{10}N^2O^4Ba$ , crystallises in needles (Griess, *J. pr. Chem.* [2], i. 233).

**URAMIDODRACYLIC ACID**,  $C^6H^3N^2O^3$ , is formed in like manner by fusing urea with anthranilic acid. When heated to  $200^\circ$  it splits up, like uramidobenzoic acid (p. 166), into urea and carboxamidosalicylic acid,  $C^8H^7N^2O^3$ :



This latter acid is nearly insoluble in water and in alcohol, and separates from its ammoniacal solution, on acidulation with hydrochloric acid, in white microscopic needles (Griess, *loc. cit.*).

**URANIUM.** *Atomic weight.*—Mendelejeff doubles the usually received atomic weight of this metal, making it 240, and regarding uranium as a hexad analogous to chromium. The reasons for this change are given in his memoir 'Ueber die periodische Gesetzmässigkeit der Chemischen Elemente' (*Ann. Ch. Pharm., Suppl.* viii. 178).

According to the atomic weight hitherto adopted (120), uranium is regarded as a metal of the iron-group, forming the oxides  $UO$ ,  $U^2O^3$ ,  $U^3O^4$ ; but it differs from the metals of this group in several important characters, viz.: that it has a high specific gravity (18.4), and forms a volatile chloride ( $UCl^4$ ); that uranic oxide does not form salts of the type  $UCl^4$  or  $U^2Cl^3$ , but only of the type  $UOX$  ( $X$  denoting an acid radicle,  $Cl$ ,  $NO^2$ , &c.); and that although uranium has a greater atomic weight than iron, it is less easily reducible, and its oxides are weaker bases than the corresponding iron oxides. Moreover, the uranous salts are not isomorphous with those of the magnesium series, as they should be if uranous oxide were a monoxide,  $UO$ . Uranous sulphate,  $UrS^2O^6 + 8H^2O$ , crystallises in the monoclinic system, and forms, according to Rammelsberg's experiments, the double salts  $\frac{2(NH^4)^2SO^4}{UrS^2O^6}$  and  $\frac{K^2SO^4}{UrS^2O^6}$ , to which there are no analogues among the sulphates of the magnesian metals (see further, Rammelsberg, *Deut. Chem. Ges. Ber.* v. 1003). On the other hand, uranium resembles the hexad metals, tungsten and molybdenum, in forming a *pentachloride* (p. 1190).

An apparent objection to the doubling of the atomic weight of uranium is, that its specific heat, 0.6190, when multiplied by 240, makes the atomic heat 14.86, which is more than double the normal value; but the force of this objection is considerably diminished by the fact that the specific heat of metallic uranium has not yet been accurately determined (see HEAT, iii. 30).

The following table exhibits the formulae of the chlorides, oxides, &c., of uranium, according to the old and new atomic weights:

U = 120

U = 240

*Uranous Compounds.*

$UCl^3$ ;  $UO$   
 $U^2SO^4 \cdot 2H^2O$   
 $K^2U^2(SO^4)^2 \cdot H^2O$

$UCl^4$ ;  $U^2O^3$   
 $U(SO^4)^2 \cdot 4H^2O$   
 $K^2U(SO^4)^2 \cdot H^2O$

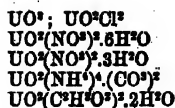
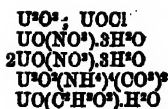
*Uranous-uranic Oxide.*

$U^2O^4 = UO \cdot U^2O^3$

$U^2O^4 = UO^2 \cdot 2UO^2$

U = 120

U = 240

*Uranic or Uranyl Compounds.*

*Estimation and Separation.*—On the titration of Uranous Solutions, see Follenius (*Zeitschr. anal. Chem.* 1872, 179).

On the Separation of Uranic from Ferric Oxide, and on the estimation of Phosphoric acid by means of Uranium, see H. Rheineck (*Dingl. pol. J.* cc. 383; *Chem. Soc. J.* [2], x. 178). On the latter point see also p. 968 of this volume.

On the working up of Uranium-residues after estimation of Phosphoric acid, see W. Jani (*Chem. News*, xxiii. 220; *Chem. Soc. J.* [2], ix. 586).

**Pentachloride,  $\text{UCl}_5$**  [U = 240] (Roscoe, *Chem. Soc. J.* [2], xii. 933). This compound is obtained, together with the well-known tetrachloride or uranous chloride,  $\text{UCl}_4$ , by passing excess of dry chlorine over a moderately heated mixture of charcoal with any of the oxides of uranium, or with the oxychloride,  $\text{UO}_2\text{Cl}_2$ . It exists in two distinct forms according as it is produced slowly or quickly. When the current of chlorine is slow, the pentachloride of uranium forms long, dark, needle-shaped crystals, which reflect light with a green metallic lustre, but appear of a splendid ruby-red colour when viewed by transmitted light. If the rate at which the chlorine passes is rapid, the pentachloride is deposited in the form of a light brown, mobile powder. The magnificent octohedral crystals of the tetrachloride are always deposited in quantity in that part of the tube nearest to the heated mixture; then the black needle-shaped crystals of pentachloride are formed, mixed with more or less of the brown powder, which is generally carried for a considerable distance along the tube. Both the black needles and the brown powder are extremely hygroscopic, yielding, on exposure to the air for a few minutes, yellowish green liquids, and hissing and giving off fumes of hydrochloric acid when thrown into water.

The mean of four analyses of this compound gave 57.47 p.c. uranium and 42.52 chlorine (= 99.79), the formula  $\text{UCl}_5$  requiring 57.49 uranium and 42.51 chlorine.

Uranium-pentachloride cannot be volatilised without partial decomposition, either when heated alone or in an atmosphere of chlorine or of carbon dioxide, uranium tetrachloride and free chlorine being formed. This dissociation begins in an atmosphere of carbon dioxide at a temperature of  $120^\circ$ , and is completed at  $235^\circ$ , when the percentage of chlorine contained in the residue shows that one-fifth of the chlorine has been driven off. The tetrachloride, when similarly heated, loses no chlorine.

The pentachloride heated to redness in a current of dry ammonia yields a black nitride.

**Uranates.** Thallous oxide added to uranium solutions forms a yellow precipitate of thallium uranate analogous to the uranates of the alkali-metals (C. Bolton, *American Chemist*, 1872, ii. 466).

**Tetraethylammonium Uranate,**  $(\text{C}^{\text{H}}^{\text{O}})^4\text{NO} \cdot \text{UO}_2 + 3\text{H}^{\text{O}}_{\text{O}}$ , is formed on adding a solution of tetraethylammonium hydroxide to a solution of uranic nitrate, as a yellow precipitate very much like that produced by ammonia, and shrinking up in drying to a brownish-red, amorphous, semivitreous mass, which yields a yellow powder. It dissolves easily in dilute acids. The acetic acid solution yields on evaporation small crystals, probably consisting of a double acetate of uranium and tetraethylammonium. On dissolving the salt in strong nitric acid, decomposition takes place (Bolton, *loc. cit.*)

On *Uranic Acetates and Sulphates*, see pp. 7, 1140.

**Uranic Arsenates.** Four of these minerals found, together with a bismuth uranate (uranospherite) in the White Hart Mine, near Schneeberg in Saxony, have been described by A. Weisbach (*Mineralogische Mittheilungen*, 1872, 181; *Jahresb. f. Mineralogie*, 1873, 296), and analysed by Cl. Winkler, with the following mean results:

	$\text{As}_2\text{O}_5$	$\text{UO}_2$	$\text{B}_2\text{O}_3$	$\text{CuO}$	$\text{CaO}$	$\text{H}_2\text{O}$	
Trögerite . . . . .	18.98	63.21	—	—	—	17.21	= 99.30
Walpurgin . . . . .	12.45	80.38	20.41	—	—	4.48	= 97.72
Zemserite . . . . .	20.94	55.86	—	7.49	—	15.68	= 99.97
Uranospinitite . . . . .	15.37	59.18	—	—	6.47	18.19	= 100.21
Uranospherite . . . . .	—	50.60	44.23	—	—	5.16	= 99.99

These analyses lead to the following formulae:

Trögerite	3UO <sup>3</sup> . As <sup>2</sup> O <sup>3</sup> + 12H <sup>2</sup> O.
Walpurgin	5Bi <sup>2</sup> O <sup>3</sup> . As <sup>2</sup> O <sup>3</sup> + 3UO <sup>3</sup> . As <sup>2</sup> O <sup>3</sup> + 10H <sup>2</sup> O.
Zeunerite	CuO . 2UO <sup>3</sup> . As <sup>2</sup> O <sup>3</sup> + 8H <sup>2</sup> O.
Uranospinito	CaO . 2UO <sup>3</sup> . As <sup>2</sup> O <sup>3</sup> + 8H <sup>2</sup> O.
Uranosphærite	Bi <sup>2</sup> O <sup>3</sup> . UO <sup>3</sup> + H <sup>2</sup> O.

*Trögerite* forms lemon-yellow monoclinic crystals, scaly by predominance of the clinopinacoid, bearing a general resemblance to the crystals of heulandite, and, like the latter, having a nacreous lustre on the clinopinacoid faces.

*Walpurgin* is mostly lemon-yellow, honey-yellow, or wax-yellow, sometimes however straw-yellow. The crystals have the character of the ordinary crystallisation of gypsum. The most highly developed faces are, as in trögerite, those of the clinopinacoid, but they have an adamantine rather than a nacreous lustre. The projecting summits of the crystals are often serrated.

*Zeunerite* forms emerald-green or apple-green quadratic crystals, of pyramidal, tabular, or scaly character, consisting of the prism, the base, and a very acute pyramid. The basal faces have a nacreous lustre, and correspond with the direction of a perfect cleavage. Zeunerite is, therefore, not only analogous in chemical composition to ordinary copper uranium mica (torbernite), but likewise isomorphous and isoclastic with it. The two minerals are, indeed, deceptively similar to one another in appearance.

*Uranospinito* forms siskin-green scaly crystals having a square or rectangular transverse section; their optical characters show that they belong to the rhombic system. The cleavage-planes run parallel to the plane of the scales, and notwithstanding the perfection of the cleavage, they exhibit but little tendency to nacreous lustre. Uranospinito probably belongs also to the family of the uranium micas, being indeed the arsenate analogous to lime-uranite (autinite).

*Uranosphærite* forms orange-yellow or egg-yellow nodules, roughly or finely drusy, and having a dull or faint satiny lustre. Under the microscope the drusy surface resolves itself into an aggregate of acutely pyramidal crystals, sticking out from the nodules like the bristles of a hedgehog. The fractured surface exhibits a fatty lustre and a concentrically scaly structure.

All five species are somewhat lighter-coloured when pulverised, and are intermediate in hardness between gypsum and calcspar. Their specific gravities, according to the mean of several determinations at 9°, are—

Trögerite	Walpurgin	Zeunerite	Uranospinito	Uranosphærite
3.23	5.64	3.53	3.45	6.36

Trögerite is therefore the lightest and uranosphærite the heaviest of the five.

With regard to succession in time, walpurgin and trögerite appear to be the oldest formations; then follows uranosphærite, then zeunerite, and lastly uranospinito.

**URANOPHANE.** A hydrated uranic silicate from Kupferberg in Silesia, having the following composition:

SiO <sup>2</sup>	UO <sup>3</sup>	Al <sup>2</sup> O <sup>3</sup>	CaO	MgO	K <sup>2</sup> O	H <sup>2</sup> O
17.08	53.38	6.10	5.07	1.46	1.85	15.11 = 100

(Websky, *Jahresb. f. Chem.* 1870, 1304).

**URANOTIL.** This is also a uranic silicate chemically and crystallo-graphically allied to uranophane, occurring in slender needles in the druses of the quartz which covers the fluor spar of Wülsendorf in Bavaria. It is lemon-yellow, blackens when heated, and dissolves in hydrochloric acid, with separation of flocculent silica. According to Zepharovich, the needles are rhombic and exhibit the faces  $\infty P$  .  $\infty P_{\infty}$  .  $mP_{\infty}$ . The angle  $\infty P$  is nearly 164°. Sp. gr. = 3.95. The mean of three analyses (A) by Boricky (*Jahresb. f. Mineralogie*, 1879, 780), and the analyses B and C by Weissbach (*ibid.* 1873, 296) lead to the formula  $UO^3.SiO^2 + H^2O$ .

	SiO <sup>2</sup>	P <sup>2</sup> O <sup>5</sup>	UO <sup>3</sup>	Al <sup>2</sup> O <sup>3</sup> .Fe <sup>2</sup> O <sup>3</sup>	CaO	H <sup>2</sup> O	
A.	13.78	0.45	66.75	0.51	5.27	12.67	= 99.43
B.	13.02	—	63.93	3.03	5.13	14.55	= 99.66
C.	14.48	—	62.84	2.88	5.19	13.79	= 99.48

**UREA, CH<sup>2</sup>N<sup>2</sup>O.** *Formation.*—Campani (*Gazz. chim. ital.*, i. 472) has observed the formation of urea by the slow evaporation of aqueous hydrocyanic acid.

*By Oxidation of Proteids.*—Béchamp, in 1856 (*Ann. Chim. Phys.* [3], xlviii. 348) described the formation of urea from albumin by the action of potassium permanganate in alkaline solution. Stædeler (*J. pr. Chem.* lxxii. 261) and O. Loew (*ibid.* [2], ii.

289), in repeating Béchamp's experiments, did not succeed in obtaining urea. Béchamp however (*Compt. rend.* lxx. 866) maintains the correctness of his former statement, and describes more fully the process by which he obtained urea from albumin. 60-70 grams of potassium permanganate are added to 10 grams of pure dry white of egg suspended in 200-300 grams of water, and the liquid is digested on a water-bath at 60°-80°. The reaction sets in after a while, with frothing, and as soon as this is over, the liquid is filtered, the precipitate washed, and the filtrate precipitated with basic lead acetate, not in excess. The lead is then removed by hydrogen sulphide, and mercuric nitrate is added to the filtered solution, which is kept nearly neutral with baryta-water till the addition of the baryta-water produces a yellow precipitate. This precipitate is suspended in water, decomposed with hydrogen sulphide; the acid filtrate saturated with barium carbonate and evaporated to dryness on the water-bath; and the residue is exhausted with alcohol of 94 p.c. The amorphous residue of the alcoholic extract gives with nitric acid crystalline laminae, which evolve gas when treated in the cold with Miller's reagents. E. Ritter (*Bull. Soc. Chim.* [2], xvi. 32) confirms Béchamp's statement, and gives the following as the quantities of urea obtained by oxidation of different proteids:

30 grams of moist Albumin gave 0.09 gram urea.

" " " Fibrin " 0.07

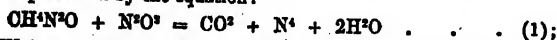
" " " Gluten " 0.29, 0.31, and 0.21 gram urea.

On the Formation of Urea in the Animal Organism, see Schulzen a. Nencki (*Zeitsch. f. Biologie*, viii. 124; *Chem. Soc. J.* [2], x. 833).

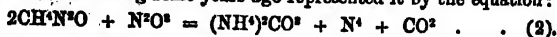
On the question whether the formation of Urea takes place in the Blood or in the Kidneys, see Gréhan (*Jahresb. f. Chem.* 1872, 916).

O. Popp (*Ann. Ch. Pharm.* clvi. 88) has obtained from fresh pig's bile, crystals which he regards as urea.

**Reactions.** 1. With Nitrous Acid.—The decomposition of urea by nitrous acid is generally represented by the equation:



whereas Wöhler a. Liebig some years ago represented it by the equation:



According to Claus (*Deut. Chem. Ges. Ber.* iv. 140) the reaction (2) takes place when nitrous acid is added to a solution of urea in the cold, in the proportion of 1 mol.  $\text{N}^+\text{O}^+$  to 2 mols. urea; reaction (1), on the other hand, when nitrous acid is gradually added to a hot solution of urea. This arises, as Wöhler a. Liebig showed, from the fact that 1 mol. urea and 1 mol. nitrous acid are resolved in the cold into cyanic acid and ammonium nitrite:



and that, on warming the solution, the ammonium nitrite is resolved into water and nitrogen, while the cyanic acid, by reacting with the water, is resolved into ammonia and carbon dioxide. When, on the other hand, the nitrous acid is gradually added, the ammonium carbonate formed in the first instance is resolved into nitrogen, carbon dioxide, and water. Equation (2) is likewise realised when a stronger acid is added to the liquid, the ammonia salt of this acid being then produced.

2. With Phosgene.—Urea, heated with excess of liquid phosgene, is converted into carbonyl-diurea,  $\text{C}^+\text{H}^+\text{N}^+\text{O}^+$ , which, by further action, yields hydrochloric acid and a mixture of cyanic, diacyanic, and cyanuric acids (p. 262).

On the action of Urea Nitrate on Benzyl Alcohol, see p. 178.

On the Detection of Urea in Blood and in the Tissues, see Perls (*Zeitschr. anal. Chem.* ix. 421; *Jahresb. f. Chem.* 1871, 1052).

On the Estimation of Urea by means of Sodium Hypobromite, see Hüfner (*J. pr. Chem.* [2], iii. 1; *Chem. Soc. J.* [2], ix. 162).

*Sulpho-ureas.* See SULPHOCARBAMIDES (p. 1116).

**URIC ACID.**  $\text{C}^+\text{H}^+\text{N}^+\text{O}^+$ . On the constitution of this acid, see Kolb (*J. pr. Chem.* [2], i. 184; Strecker, *Ann. Ch. Pharm.* clv. 177; also *Jahresb. f. Chem.* 1870, 724).

On the Estimation of Uric acid in Urine, see E. Salkowski (*Pflüger's Archiv. f. Phys.* v. 210; *Deut. Chem. Ges. Ber.* v. 410; *Chem. Soc. J.* [2], x. 383, 844; H. Schwarzenb., *Ann. Chem. Pharm.* clxiii. 163; *Deut. Chem. Ges. Ber.* v. 316; *Chem. Soc. J.* [2], x. 844, 929; R. Maly, *Pflüger's Archiv.* v. 301; *Chem. Soc. J.* [2], ix. 1123).

**URICIN.** (Neubauer a. Vogel, *Anleitung zur qual. u. quant. Anal. d. Harns.* 6. Auflage). Thudichum (*Centr. f. d. Med. Wissen.* 1870, No. 13, 14; *Chem. Soc. J.* [2], viii. 132) has described an amorphous nitrogenised acid,  $\text{C}^+\text{H}^+\text{N}^+\text{O}^+$ , which he names cryptophanic, as a normal constituent of human urine (see *lit. Suppl.* 213). See



observers have however completely failed to prepare this acid, and are agreed that Thudiechum's calcic cryptophanate is a variable mixture of still unknown bodies, whose indefiniteness and impurities render it impossible to make as yet any definite assertion as to their composition (see Fucher, *Centr. f. d. Med. Wissen.* 1871, 22, and Liversidge, *Journ. of Anat. a. Phys.* May 1872). Thudiechum has however repeated his statement (*Centr. f. d. Med. Wissen.* 1872, 81), and also described another acid with the composition  $C^{11}H^{10}N^{10}O$ , which he calls *paraphanic*, as existing in the mother-liquor from which the calcic cryptophanate has been precipitated. He also believes that he has detected acetic acid as a normal constituent of human urine (*Deut. Chem. Ges. Ber.* 1870, 578).

Roberts (*Mem. Manch. Lit. a. Phil. Soc.* 1862) has given a simple method of estimating the quantity of sugar in urine, which is extremely useful as being sufficiently accurate for clinical purposes. The specific gravity of the urine is taken, and a little dried yeast is added to it; it is then set aside in a warm place for 24 hours, and its specific gravity is again taken; the number of degrees of specific gravity which is lost answers to one grain of grape-sugar in a fluid ounce of urine, or multiplied by 0.23, will give the number of parts of sugar in 100 of the urine. According to Hensley, the quantity reckoned in this way is, on theoretical grounds, about  $\frac{1}{8}$  too great. Manassein finds that for practical purposes it may be regarded as very nearly exact (*Deutsches. Arch. f. Klin. Med.* 1872, 73); the number which he gives as multiplier is 0.219. With reference to the detection of grape-sugar in urine by means of Trömmner's test, it is worthy of note that the reaction is much clearer if the urine be previously filtered through animal charcoal; in many cases indeed, even when a considerable quantity of glucose is present, no reduction will occur on boiling, unless this precaution be taken previously. The animal charcoal holds back a very small quantity of the glucose.

The exact places in the body at which urea is formed are still far from accurately known. It has already been pointed out that there is considerable reason to believe that a good deal is formed in the liver (see GRAYCOCK), but many observers still maintain that all, or nearly all, is formed in the kidneys, from less highly oxidised nitrogenous compounds brought to them by the blood. Voit has shown that creatine when introduced into the blood passes out in the urine as creatinine, and not as urea, and he has also shown that, after extirpation of the kidneys, just as much urea accumulates in the blood and organs as after simple ligature of the ureters (*Sitz. d. Kön. bayer. Acad. d. Wiss.* 1867, i. 364; see also Gréhant, *Journ. de l'Anat. et de la Phys.* 1870, 318). These facts very strongly support the view that urea is simply separated from the blood in the kidneys. It has also now been well established that muscular work has little or no effect on the excretion of nitrogen in the urine (see MUSCULAR TISSUE), but that, on the other hand, the quantity of proteid matters taken in the food has a very important influence. Possibly in the latter case a good deal of the urea proceeds almost directly from the food, for it has been shown that leucine, which is largely formed in the small intestine from proteid foods, is, when given to an animal, excreted for the most part as urea (Schultzen u. Nencki, *Zeitsch. f. Biologie*, 1872, 189). Glycine and glycocine, when administered to an animal, also increase the quantity of urea excreted by it. There is also much reason to believe that a good deal of urea is formed in the spleen (Gscheidlen, *Ueber den Ursprung des Harnstoff's im Thierkörper*, Leipzig, 1871).

Reysson (*Journ. pour l'Anat. et Phys.* p. Robin. 1872, 388) has suggested that the acidity of normal human urine is not due, as generally supposed, to the presence of acid phosphates, but rather to free uric and hippuric acids, since he finds that those bodies cannot decompose neutral sodic phosphate at ordinary temperatures.

H. N. M.

**UROBILIN.** See BILE-PIGMENTS (p. 190).

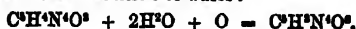
**UROSULPHINIC ACID,  $C^4H^4N^1SO^2$ .** This name is given by Nencki (*Deut. Chem. Ges. Ber.* v. 45) to an acid produced by the action of strong sulphuric acid on sulpho-pseudo-uric acid (p. 1125) at a temperature not exceeding  $160^\circ$ . The substance precipitated by water is dissolved in ammonia, reprecipitated by hydrochloric acid, and the washed and dried precipitate is boiled with a weak alkaline-ley. The alkali salt then separates from the filtrate in white needles containing water, and may be purified by repeated crystallisation. The acid precipitated from it by hydrochloric acid and dried at  $140^\circ$  has the composition above stated.

Urosulphinic acid is intermediate in its chemical relations between uric acid and xanthine. It is a weak monobasic acid, and is precipitated from its alkaline solution by carbonic acid in characteristic spherical forms. The sulphur is not abstracted from it by metallic oxides at the boiling heat or even at higher temperatures. The acid is decomposed by prolonged boiling of its alkaline solution, but it is not altered by heat.

ing it to 200° with water for five hours. Sodium-amalgam converts it into a sulphuretted compound which dissolves easily in hot water and crystallises in silky needles.

**UROXANIC ACID.** This acid, which Städelcr obtained by the action of potash on uric acid (v. 969), has been further examined by Strecker (*Ann. Ch. Pharm.* clv. 177). To prepare it, uric acid was dissolved in potash-ley, and left to itself, in a flask fitted with a potash tube. In about six months the uric acid was decomposed, and the solution, cooled to between -5° and -10°, deposited crystallised potassium uroxanate, from which the uroxanic acid was precipitated by hydrochloric acid.

Analyses of the acid and its salts led to the formula  $C^9H^4N^4O^8$ , whereas Städelcr found  $C^9H^4N^4O^8$ . From Strecker's formula it appears that uroxanic acid is formed from uric acid by oxidation and addition of water:



*Potassium Uroxanate*,  $C^9H^4K^1N^4O^9$  +  $3H^2O$ , or  $3\frac{1}{2}H^2O$ , does not give off all its water of crystallisation till it begins to decompose. The *silver salt*,  $C^9H^4Ag^1N^4O^9$ , obtained from it by precipitation, is a white crystalline powder. The *barium salt*,  $C^9H^4Ba^1N^4O^9$  +  $5H^2O$ , prepared in like manner, gives off its water at 100°-110°. The *calcium salt*,  $C^9H^4Ca^1N^4O^9$  +  $4H^2O$ , similarly prepared, dissolves in hot water and separates, on addition of alcohol, in white needle-shaped crystals.

**USNIC ACID**,  $C^{11}H^{10}O^7$  (Stanhouse, *Proc. Roy. Soc.* xviii. 222). *Preparation from Usnea barbata*.—This lichen is macerated with a dilute solution of sodium carbonate, and the crude dark green acid, precipitated from the turbid solution by hydrochloric acid, is mixed with milk of lime and warm water at 40°. From the clear lemon-yellow filtrate the usnic acid is precipitated by hydrochloric acid in pale yellow flocks.

*Sodium usnate* forms pale yellow silky needles, not very soluble in cold water, more soluble in alcohol; it is easily decomposed by carbonic acid. The *calcium salt*, which separates from a boiling solution, is also completely decomposed by carbonic acid.

Usnic acid, identical with that from *Usnea barbata*, is likewise obtained from *Xeraria prunastri*, in which it exists together with evernic acid (p. 496). The two acids extracted from the lichen by milk of lime are precipitated together by hydrochloric acid, and the dried precipitate is treated with boiling alcohol, which dissolves the evernic acid, and leaves the usnic acid, which may be purified as above.

Usnic acid is isomeric with cladonic ( $\beta$ -usnic) acid (p. 353). The two acids are distinguished by their melting points, usnic acid melting at 202°, cladonic acid at 176°. Moreover cladonic acid, when subjected to dry distillation, yields  $\beta$ -orcin (iv. 204), whereas pure usnic acid yields none.

## V

**VACCINIUM.** The fruit of the red whortleberry (*Vaccinium Vitis Idæa*) has been examined by Grägr (*N. Jahrb. Pharm.* xxxvi. 208) according to the method for the examination of fruits given by Fresenius (ii. 712, 716). The juice obtained from the crushed perfectly ripe berries, by four times repeated exhaustion with distilled water, was found to contain:

Free acid, reckoned as malic (better, however, as citric acid)	1.97	Potash	0.06
Fruit-sugar	5.18	Lime	0.13
Tannic acid	0.48	Magnesia	0.01
Proteids (pectin-substances), sus- pended fat, &c.	2.33	Ferric oxide	0.02
		Water	89.81

The berries yielded 10.18 p.c. soluble substances, 85.61 p.c. water, and 4.20 p.c. residue, dried at 100°, which contained 0.1 p.c. ash. The free acid is chiefly citric, with a little malic acid. The proportion of ferric oxide is unusually large. For concentrating the juice Grägr recommends the addition of 5 or 6 grams of sodium bicarbonate to 0.5 kilos. of whortleberries.

*Vaccinin*.—This name is given by E. Claassen (*Arch. Pharm.* [2], cxlv. 248) to a slightly bitter inodorous non-nitrogenous substance which he obtained from the whortleberries by boiling the fresh plants in water with a little milk of lime, &c. It crystallises in long colourless silky needles, melts when heated, is not precipitated from its solutions by basic lead acetate or tannic acid.

**VALERAL** or **VALERIC ALDEHYDE**,  $C^5H^{10}O$ . 1. **Normal Valeral**,  $CH^3-(CH^2)^4-CHO$ , prepared from normal valeric acid by distilling the calcium salt with an equivalent quantity of calcium formate, and purified by fractional distillation, boils at  $102^\circ$ , dissolves completely in a large quantity of water, and forms a crystalline compound with sodium bisulphite (Lieben & Rossi).

2. **Isovaleral. Ordinary Valeric Aldehyde**,  $\begin{matrix} H^1C \\ H^2C \end{matrix} > CH-CH^2-CHO$  (A. Schröder,

*Deut. Chem. Ges. Ber.* iv. 400, 468). This compound boils at  $92.5^\circ$  under a barometric pressure of 758.2 mm. Sp. gr. = 0.768 at  $12.5^\circ$ . Vapour-density = 43.06 ( $H = 1$ ; calc. = 43).

**Valeral-ammonium**,  $C^5H^9(NH^4)O$ , exhibits the normal vapour-density. A determination at  $160^\circ$  gave the value 52.16; calc.  $51.5^\circ$ . ( $H = 1$ ). The vapour-density of the hydrated compound,  $C^5H^9(NH^4)0.7H^2O$ , is by experiment 14.31, which is also normal; for the 7 mols. of water occupy 14 volumes, and if the group  $C^5H^9(NH^4)O$  occupies two volumes, the hydrated molecule should occupy 16 volumes, and the molecular weight 220, divided by 16, gives 14.5, which is nearly the same as 14.31.

**Action of Chlorine on Valeral.**—When chlorine is passed into valeral, first in the cold, afterwards at  $145^\circ$ , as long as it is absorbed, the compound  $C^5H^9Cl^2O$  is formed according to the equation:

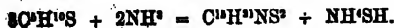


This body, which may be regarded as a derivative of the condensation-product,  $C^5H^{10}O$  (p. 1196), is a liquid having a fetid odour like that of the goat, and boiling at  $203^\circ-204^\circ$ . It does not combine with alkaline bisulphites, and is not acted upon by cold nitric acid. Boiled with fuming nitric acid it yields a nitro-derivative. On treating it with a boiling solution of caustic soda in alcohol, 2 mols. of hydrochloric acid are taken out, and the body  $C^5H^9Cl^2O$  is obtained, which is an oily liquid having a pleasant smell of mint, and boiling at  $208^\circ-210^\circ$ .

**Chlorovaleral**,  $C^5H^9ClO$ , is formed, together with more highly chlorinated products, when valeral is imperfectly saturated with chlorine in the cold. It is a liquid boiling at  $134^\circ-135^\circ$ , and forming crystalline compounds with alkaline bisulphites.

**Thiovaleral**,  $C^5H^9S$ .—Dry hydrogen sulphide does not act upon valeral, but when this gas is passed into its aqueous solution, white crystals separate, consisting of thiovaleral. This compound is insoluble in water, soluble in alcohol and ether, and separates from a hot ethereal solution in asbestos-like crystals. It has a most offensive and persistent odour, melts at  $69^\circ$ , and, when heated very strongly, decomposes, giving off white fumes having an indescribable smell; but it may be sublimed without decomposition in a vacuum. Vapour-density, obs. = 50.76; calc. = 61.

**Valeraldine**,  $C^5H^9NS$  (v. 974), is formed by passing dry ammonia over thiovaleral:



Thus prepared it contains an excess of ammonia, which may be removed by a current of hydrogen, or by dissolving it in ether and evaporating the solution in a vacuum over sulphuric acid. It is thus obtained as an oil, which, by standing over sulphuric acid in a vacuum for some time, and being then exposed for a short time to the air, becomes crystalline. The oily valeraldine may also be solidified by passing hydrocyanic acid over it. It melts at  $41^\circ$ , and is a very indifferent body, not being acted upon by hydrocyanic acid, cyanogen gas, or cyanogen chloride; it is insoluble in water, soluble in alcohol or ether; from the latter it crystallises in white fern-like leaves, having the consistence of wax. Its odour resembles that of acetamida. When heated, it distils with decomposition; but in a vacuum it sublimes undecomposed.

**Seleniovaleral**,  $C^5H^9Se$ , obtained by passing hydrogen selenide into the aqueous solution of valeral, is a crystalline solid, which cannot be re-crystallised, as its solution in ether, alcohol, or methyl-alcohol soon decomposes, with separation of selenium in the form of a mirror; but it may be purified, as it volatilises in a current of gas with aqueous vapour at the common temperature. It forms white crystalline crusts, melting at  $56.5^\circ$ ; its odour is exceedingly offensive, and produces difficulty of respiration and palpitation of the heart. It decomposes at  $30^\circ$  in contact with mercury. With dry ammonia it forms seleniovaleraldine, a compound closely resembling valeraldine (Schröder).

**Carbovaleraldine**,  $C^5H^9N^2S$ , is formed either by shaking a mixture of carbon



formed from the iodopropionic acid in question is not normal valeric or propyl-acetic acid, but methyl-ethyl-acetic acid. Respecting *trimethyl-acetic acid*, see p. 1182.

**Normal Valeric, Propyl-acetic, or Butyl-formic Acid,**  $\text{CH}_3(\text{CH}_2)_3\text{COOH}$  (Lieben & Rossi, *Gazzetta chimica italiana*, i. 239). This acid is formed by oxidation of normal amyl alcohol, and by distilling normal butyl cyanide with alcoholic potash in a retort with reversed condenser as long as ammonia continues to escape. On distilling off the alcohol (which contains ammonia and a mixture of mono-, di-, and tri-butylamine, formed as secondary products), dissolving the residual saline mass in water, saturating approximately with sulphuric acid, filtering to separate potassium sulphate, evaporating the filtrate to dryness, and treating the residue with dilute sulphuric acid, the valeric acid is separated and rises as an oil to the surface. This oily liquid washed with a little water and distilled, rejecting the first few drops, which are slightly humid, yields pure valeric acid boiling within an interval of  $1.5^\circ$ , and yielding by analysis 58.63 p.c. C., and 9.62 H., the formula  $\text{C}_5\text{H}_{10}\text{O}_2$  requiring 58.82 C., and 9.80 H.

Normal valeric acid has an odour more like that of pure butyric acid than that of ordinary valeric acid. It boils at  $184^\circ\text{--}185^\circ$  (corr.) under a pressure of 736 mm. When cooled to  $-16^\circ$ , it becomes slightly viscous, but does not solidify. A cubic centimeter of this acid dissolves at  $16^\circ$  about 1 c.c. of water; on adding more water, a lower aqueous layer is formed, on which the valeric acid floats, but after the addition of 27 c.c. water to 1 c.c. acid, complete solution takes place. The specific gravity of normal valeric acid referred to water at the same temperature is as follows:—

Temperature	0°	20°	40°	99.3°
Specific gravity	0.9577	0.9415	0.9284	0.9034

**Normal Valerates.**—All the following salts were prepared by saturation, excepting the copper salt, which being but sparingly soluble, was obtained by precipitation. The *sodium salt* is very soluble in water, and the hot solution gelatinizes on cooling. The *barium salt*,  $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Ba}$ , is more soluble in hot than in cold water, and its hot saturation solidifies on cooling to a mass of unctuous laminar crystals. The dry salt, obtained by evaporating the solution at ordinary temperatures and exposing the crystals to the air, is neutral and anhydrous. 100 pts. of a solution saturated at  $10^\circ$  contain 16.906 pts. of the anhydrous salt. The *calcium salt* is obtained by evaporation at ordinary temperatures in small, shining, unctuous laminae, resembling those of the barium salt; they contain  $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Ca} + \text{H}_2\text{O}$ , and give off their water of crystallisation at  $100^\circ$ . This salt exhibits a maximum of solubility at about  $70^\circ$ , so that it separates from a hot saturated solution on cooling, and from a cold saturated solution on heating. A solution saturated at about  $20^\circ$  contains 8.0809 p.c. of the anhydrous salt. The *manganous salt*,  $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Mn} + \text{H}_2\text{O}$ , forms small faintly rose-coloured crystals, which give off their water at  $100^\circ$ . It is much more soluble in cold than in hot water, and a solution saturated in the cold deposits, when heated, a precipitate (probably of basic salt) which does not redissolve completely on cooling; this decomposition by heat takes place with especial facility in dilute solutions, so that such solutions cannot be concentrated by heat.

The *cupric salt*,  $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Cu}$ , is obtained, by precipitating the sodium salt with cupric sulphate, as an azure-green substance, which partly dissolves when washed and digested with water at ordinary temperatures. The resulting sky-blue solution, when evaporated in a vacuum over sulphuric acid, yields the neutral salt in groups of green microscopic needles; its powder has a lighter colour inclining to sky-blue. This salt is likewise more soluble in cold than in hot water, its solution becoming turbid when heated, and always depositing a small quantity of basic salt, which does not redissolve on cooling; and on evaporating the solution by heat, a residue is obtained consisting chiefly of a sky-blue basic salt. On boiling a dilute solution of the neutral salt, or heating a solution of the basic salt, cupric oxide is precipitated, and valeric acid volatilises with the aqueous vapour. The same decomposition appears also to take place partially at ordinary temperatures. The *zinc salt*,  $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Zn}$ , forms thin, shining, transparent laminae, unctuous to the touch. 100 pts. of a solution, saturated at  $24\text{--}26^\circ$ , contain 2.64 pts. of the salt; the solution becomes turbid when heated, but the precipitate redissolves on cooling.

**Isovaleric, Isopropyl-acetic, or Isobutyl-formic Acid,**  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ . **Ordinary Valeric Acid.**—The properties of this acid and its salts, as obtained from various sources, have been carefully studied by Erlenmeyer & Hell (*Ann. Ch. Pharm.* clx. 267).

1. **Valeric Acid, prepared by boiling Isobutyl Cyanide with Alcoholic Potash.**—The acid thus prepared is a colourless, oily, optically inactive liquid, which makes a white spot on the tongue. The *silver salt* crystallises from neutral solutions in dendritic bundles,

from solutions containing a little free acid, especially acetic acid, in large, highly lustrous, apparently triclinic laminae. It is sparingly soluble in cold water, more soluble in hot water, and in water containing free fatty acids. It is permanent in the air, and not much altered by light. The crystals rotate rapidly on dilute nitric acid. The barium salt crystallises in anhydrous prisms or laminae belonging to the triclinic system; they are permanent in the air, and rotate quickly on water. The aqueous solution decomposes gradually at ordinary temperatures, more quickly on boiling, giving off valeric acid.

2. From *Valerian root*.—The crude acid contained formic acid, acetic acid, and an acid boiling at 180°–195°, but not butyric acid; it was dextrogyrate, but by recrystallisation of the barium salt, a perfectly inactive acid was obtained. The silver and barium salts resemble those of the acid from isobutyl cyanide.

3. From *Amyl Alcohol*.—The separation of the active and inactive amyl alcohols was effected by Pasteur's method, depending on the difference of solubility of the corresponding amylsulphates of barium (i. 203). The valeric acid prepared from the inactive alcohol, when purified by recrystallisation of its barium salt, and separation therefrom, was absolutely destitute of rotatory power, and agreed in other respects with the acids prepared from isobutyl cyanide and from valerian root. The valeric acid prepared from the active amyl alcohol (too small in quantity for complete purification) boiled for the most part between 168° and 171°. Rotatory power = +30° to 40°. The silver salt crystallises from acid solution in laminae, from neutral solution in felted feathery crystals. The barium salt remains on evaporation as a thick syrup which often only after some months deposits small crystals resembling those of the barium salt above described. The syrupy mother-liquor scarcely wets paper, so that the crystals cannot be freed from it either by absorption or by pressure; it dries up to a varnish. The solution of the salt dialyses with peculiar facility through parchment paper. The salt dissolves in all proportions in alcohol, but is insoluble in ether.

The separation of active valeric acid from a mixture of the two cannot be completely effected by crystallisation of their barium salts, or by fractional distillation, or by partial oxidation of a mixture of the two alcohols. Erlenmeyer & Hell found, however, in a commercial product consisting of a mixture of amyl valerate and amyl alcohol (residues of the preparation of valeric acid) a material for the preparation of very active valeric acid. The acid obtained from it by saponification of the valeric ether had a rotatory power = +48.7°, and boiled at 172.5°–173.5° under a pressure of 721 mm.

Valeric acid, active or inactive, is easily oxidised by a mixture of 2 mols. water, 1 mol. strong sulphuric acid, and as much potassium dichromate as can dissolve therein at 20°. The products are acetic acid, carbon dioxide, and water. If the inactive acid were isobutyl-formic acid, its oxidation would probably take place according to the equation:



yielding 123.9 p.c. CO<sub>2</sub>. The acid from inactive amyl alcohol actually yielded 120.04, and that from valerian root 123.4 p.c. CO<sub>2</sub>. The quantity of carbonic acid produced by oxidation of the active acid was too variable to give any distinct indication of its constitution.

The active acid, heated for a quarter of an hour with a few drops of strong sulphuric acid, becomes optically inactive without alteration of its other properties.

4. From *Leucine*.—The cold saturated solution of leucine, prepared by boiling elastic tissue or various proteids with dilute sulphuric acid, is optically inactive. The valeric acid obtained by heating it with a mixture of potassium dichromate or manganese dioxide and sulphuric acid, or by fusing it with potash, was too small in quantity to be completely purified; it contained a little acetic acid. Its rotatory power was +17°. The barium salt showed little tendency to crystallise, and it was impossible to decide whether it consisted of a single salt or of a mixture of two.

Erlenmeyer & Hell are of opinion that valeric acid obtained from valerian root, or by oxidation of amyl alcohol, or of leucine from various proteids, is almost always a mixture in various proportions of two acids, one of which is inactive isobutyl-formic acid, while the other is the optically active acid, whose barium salt is more soluble and less easily crystallisable than that of the inactive acid.

The following table exhibits a comparative view of the properties of the valeric acids from the four sources above mentioned. The specific gravity in each case is referred to water at the same temperature. The optical rotation is given for a column 50 cm. thick, in degrees or divisions of a Ventke's saccharimeter. The properties of normal valeric acid, as determined by Lieben & Rosol, are also given for comparison.

**VALERIO ACID.**

Valeric Acid from						
	Normal Valeric Acid	Isobutyl Cyanide	Valerian Root	Amyl Alcohol:		Lendine
				Inactive	Active	
Boiling point . . . . .	184°-185° corr. under 736	172-6°-174-1° corr. bar. at 722-5 mm.	173-2°-174-3° corr. bar. at 718-3 mm.	171-5° corr. bar. at 721 mm.	172-5°-173-5° corr. bar. at 721 mm.	168°-171° corr. bar. at 720-8 mm.
Specific gravity . . . . .	0-9577 at 0° 0-9415 at 20°	0-9471 at 0° 0-9307 at 19-7°	0-9455 at 0° 0-9309 at 18-9°	0-9455 at 0° 0-9206 at 20-2°	0-9264 at 0° 0-9133 at 19-5°	— —
Optical rotation . . . . .	0	0	0	0	+ 48-7°	+ 17°
100 pts. water dissolve of the silver salt . . . . .	—	0-185 pt. at 21°	0-186 pt. at 20°	0-185 pt. at 20-5°	0-195 pt. at 22°	0-191 pt. at 21°
Crystallisability of barium salt . . . . .	crystallises easily; anhydrous	crystallises easily; anhydrous	crystallises easily; anhydrous	crystallises easily; anhydrous	not crystallisable, either from water or from alcohol	the same
100 pts. aqueous solution contain of the barium salt . . . . .	16-906 pts. at 10°	40 pts. at 22°	46 pts. at 13°	48-4 pts. at 18°	—	apparently soluble in all proportions
100 pts. of alcoholic solution contain of the barium salt . . . . .	—	14-6 pts. at 21°	13-9 pts. at 19-5°	14-4 pts. at 21°	—	—
100 pts. of absolute alcoholic solution contain of the barium salt . . . . .	—	3-3 pts. at 19-5°	2-7 pts. at 19-5°	3-5 pts. at 19-5°	—	—
CO <sub>2</sub> evolved by oxidation of the acid . . . . .	—	—	123-4 p.c.	120-4 p.c.	93-7 p.c. 102-8 " 96-6 " 98-4 "	—

According to Pierre a. Puchot (*Compt. rend.* lxxv. 1005) valeric acid obtained by oxidation of ordinary amyl alcohol, boils at  $178^{\circ}$  under a pressure of 760 mm. and exhibits the following specific gravities:

Sp. gr.	0.9470	0.8972	0.8542	0.8095
at	$0^{\circ}$	$54.65^{\circ}$	$99.9^{\circ}$	$147.5^{\circ}$

A mixture of the concentrated acid with water boils regularly between  $99.8^{\circ}$  and  $100^{\circ}$ , giving off vapours which condense to two layers, the upper of which is the pure acid, and the lower its aqueous solution.

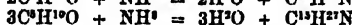
Ordinary calcium valerate separates from its solution at ordinary temperatures in crystals containing 3 mols. water (Barone, *Deut. Chem. Ges. Ber.* iv. 758).

Zinc valerate unites with ammonia, forming the compound  $(C^4H^9O^2)_2Zn.2NH_3$  (*Monatsh.* lxx. v. 30).

**VALERATES.** Pierre a. Puchot (*Ann. Chim. Phys.* [4], xx. 234) have determined the boiling points and densities of the ordinary valerates of methyl, ethyl, and butyl (from fermentation butyl alcohol), with the following results:

	Methyl Valerate, $C^4H^9O^2.CH^3$	Ethyl Valerate, $C^4H^9O^2.C^2H^5$	Isobutyl Valerate, $C^4H^9O^2.C^4H^9$
Boiling point	$117.25^{\circ}$ at 755 mm.	$135.5^{\circ}$ at 760 mm.	$173.4^{\circ}$ at 760 mm.
Specific gravity at	$0^{\circ} = 0.9005$	$0^{\circ} = 0.886$	$0^{\circ} = 0.8884$
	$41.5^{\circ} = 0.8581$	$55.7^{\circ} = 0.832$	$49.7^{\circ} = 0.8438$
	$64.3^{\circ} = 0.8343$	$99.63^{\circ} = 0.7843$	$100^{\circ} = 0.7966$
	$100.1^{\circ} = 0.7945$	$122.5^{\circ} = 0.7582$	$155.8^{\circ} = 0.7428$
Odour	like bananas	like rennet apples and <i>Mentha aquatica</i> ; excites coughing	like the ethylic ether

**VALERIDINE**,  $C^6H^{12}N$ , and **VALERITRINE**,  $C^{10}H^{20}N$ . Two volatile bases obtained by the action of alcoholic ammonia on valeral at  $150^{\circ}$ . Their formation takes place in the manner shown by the following equations:



Valeridine hydrochloride crystallises in laminae; valeritrine forms a characteristic picrate (Ljubarin, *Deut. Chem. Ges. Ber.* iv. 976; v. 1101).

**VALERONITRIL**,  $C^4H^7N$ , is formed, together with valeramide, by heating valeric acid with potassium sulphocyanate. It boils at  $125^{\circ}$ – $128^{\circ}$ . Fuming nitric acid converts it into a crystalline compound not yet examined (Letts, *Deut. Chem. Ges. Ber.* v. 669).

**VANADIUM.** This element has been found in trap-rocks by R. Apjohn (*Chem. Soc. J.* [2], x. 1116), and in iron ores from the county of Antrim in Ireland, by R. J. Hodges (*Chem. News*, xxvi. 238).

**Vanadates.** *Eosite.*—This name is given by A. Schrauf (*Jahrb. f. Mineralogie*, 1871, 163, 451) to a quadratic, aurora-red mineral implanted on cerussite at Leadhills, and regarded as a species intermediate between molybdate and vanadate of lead. The crystals exhibit the forms OP and P, the latter =  $62.50^{\circ}$ . Streak brownish-yellow. Hardness = 3.

*Vanadinite*,  $3(VO^4)Pb^2.PbCl^2$ .—On the artificial formation of this mineral, see 1st Suppl. 1125.

Maskelyne a. Flight (*Chem. Soc. J.* [2], x. 1053) found in a vanadinite from South Africa (sp. gr. 6.61):

Pb.	VO	Cl
78.416	19.829	2.56
77.770	18.670	undetermined

The absence of Mo, Cr, and P was directly established.

The relations between vanadinite, descloizite, and dechenite have been examined by A. Schrauf (*Jahrb. f. Mineralogie*, 1871, 638; *Chem. Soc. J.* [2], ix. 400). Of the two varieties of vanadinite from Bannal, the darker is identical with descloizite from Peru, while the lighter is nearly related crystallographically to descloizite, chemically to the dechenite of Niederschleissbach.



*Vanadiolite*.—A mixture of calcic hypovanadate with augitic substance, found, together with lawrowite, near Lake Baikal (see LAWROWITZ, p. 726).

**VANILLIC ACID** or **VANILLIN**,  $C^8H^8O^3$ . The odorous principle of vanilla, the fruit of *Vanilla planifolia*, has been the subject of various contradictory statements. Gobley assigned to it the formula  $C^{10}H^{10}O^3$ ; Stokkebye regarded it as  $C^{10}H^{10}O^{13}$  (v. 994). W. v. Leutner (*Russ. Zeitschr. Pharm.* x. 641, 676, 706; *Jahresh. f. Chem.* 1871, 816) regards it as a neutral substance, *vanillin*, having the composition  $C^8H^{10}O^3$ , and states that when boiled with potash-ley it takes up water and is converted into a monobasic acid, *vanillic acid*,  $C^8H^{10}O^4$ , the silver salt of which contains  $C^8H^{13}AgO^4$ .

The true composition of vanillic acid has been determined by P. Carles (*Bull. Soc. Chim.* [2], xvii. 12), who has described and analysed many of its derivatives. The vanillic acid, which forms an efflorescence on the surface of the ripe fruit, and is at the bottom of the vessels in which they are kept, was dissolved in water, decolorised by animal charcoal, and several times recrystallised. By slow cooling it separates in large translucent prisms, which may attain a length of more than 2 cm. It has a pungent taste, and when fresh and pure, only a faint aromatic odour, which, however, becomes stronger on warming. It melts between  $80^\circ$  and  $90^\circ$ , and may be sublimed, but when distilled from a tube, passes over with distillation at  $280^\circ$ , and becomes partially resinised. It is very soluble at ordinary temperatures in alcohol, ether, chloroform, carbon sulphide, and oils, gives off 1.2 p.c. water at  $15^\circ$ , and a very large quantity at boiling heat. It decomposes carbonates and saturates alkaline bases completely at ordinary, and alkaline earths at higher temperatures. Its *lead*, *magnesium*, and *zinc salts*,  $(C^8H^9O^4)^2M$ , are sparingly soluble in water, and are obtained by precipitation. The lead salt is decomposed by boiling water into a more soluble acid salt and resinous basic salts. These salts are but little altered by exposure to the air, but the ammonium, potassium, sodium, barium, and calcium salts quickly turn brown in contact with the air, and leave a blackish indistinctly crystalline residue when their solutions are left to evaporate in a vacuum.

*Bromovanillic acid*,  $C^8H^7BrO^4$ , is formed by adding bromine in slight excess to a concentrated lukewarm aqueous solution of vanillic acid—taking care to prevent rise of temperature—as a precipitate which, after crystallisation from alcohol, and finally from boiling water, with addition of animal charcoal, forms nacreous, scentless, light yellow crystals, which dissolve sparingly in cold water, more easily in alcohol, ether, and chloroform, melt at  $161^\circ$ , and sublime without decomposition. The mother-liquor contains more highly brominated products.

*Mono-iodovanillic acid*,  $C^8H^7IO^4$ , obtained by adding alcoholic iodine to aqueous vanillic acid, forms white nacreous crystals which, after two recrystallisations from alcohol, melt at  $174^\circ$ , sublime undecomposed, and have a faint odour. *Di-iodovanillic acid*,  $C^8H^6I_2O^4$ , obtained by using an excess of iodine, forms nacreous crystals slightly soluble in boiling water, insoluble in cold chloroform, soluble in warm alcohol and ether.

With *chlorine*, vanillic acid does not form any crystallised substitution-products.

*Action of melting Potash on Vanillic acid*.—When vanillic acid is gradually added to melting potash, the cooled mass treated with strong hydrochloric acid, the whole then shaken with ether, and the ethereal solution left to evaporate, small warty crystals are obtained of a compound regarded by Carles as oxyvanillic acid. This substance, after two crystallisations from boiling water, forms white, scentless, prismatic crystals melting at  $169^\circ$ , slightly soluble in cold, very soluble in boiling water, soluble in alcohol and in ether. It saturates bases completely, and some of its salts are crystalline. Its solution does not alter the colour of pure ferrous salts, but in presence of traces of ferric oxide, a very deep green colour is produced, which is destroyed by nitric acid, chlorine, and sulphurous acid.

*Action of Hydriodic acid*.—Vanillic acid, heated to  $100^\circ$  in a sealed tube for 30 hours with five times its weight of fuming hydriodic acid, forms a brown product which, on distillation, yields methyl iodide (Carles).

*Formation of Vanillic acid from Conifera*.—When coniferin,  $C^{14}H^{22}O^4$ , the glucoside contained in the cambium of coniferous woods (*1st Suppl.* 480), is digested at  $26^\circ$ – $36^\circ$  with water and a small quantity of emulsin, it splits up into glucose and a substance which separates in white crystalline floccs, and, after purification by solution in ether, has the composition  $C^8H^{10}O^4$ . This substance acquires the odour of vanilla on exposure to the air, and when it is oxidised with chromic acid mixture, the product on shaken with ether, and the ether left to evaporate, there remains an oil which, on cooling, solidifies to a substance identical in composition, melting point, and all its

other properties, with vanillic acid from vanilla, forming the same salts, and the same bromine- and iodine-derivatives (Tieman & Haarmann, *Deut. Chem. Ges. Ber.* vii. 608).

When coniferin, the crystalline substance  $C^{10}H^{10}O^8$ , or vanillic acid, is fused with potash, protocatechuic acid is formed, and vanillic acid heated with hydriodic acid yields methyl iodide. Hence vanillic acid may be inferred to be a methylic ether of

protocatechuic aldehyde, viz.  $C^8H^8 \begin{pmatrix} OCH^3 \\ OH \\ COH \end{pmatrix}$ . This aldehyde has not been actually

separated from the products of the action of hydriodic acid on vanillic acid, but it is formed, together with methyl chloride, when vanillic acid is heated to  $180^\circ$ – $200^\circ$  with dilute hydrochloric acid. With *acetic anhydride* vanillin yields acetyl-vanillic

acid,  $C^8H^8 \begin{pmatrix} OCH^3 \\ OC^2H^3O \\ COH \end{pmatrix}$ , and with *benzoyl chloride* it yields benzoyl-vanillic

acid,  $C^8H^8 \begin{pmatrix} OCH^3 \\ OC^7H^7O \\ COH \end{pmatrix}$ .

The substance  $C^{10}H^{10}O^8$  is probably a methyl-ethylic ether of protocatechuic aldehyde, or an ethylic ether of vanillic acid, and may be represented by the formula

$C^8H^8 \begin{pmatrix} OCH^3 \\ OC^2H^3 \\ COH \end{pmatrix}$ , this view being confirmed by the fact that hydriodic acid decomposes

the substance, with formation of methyl iodide and ethyl iodide. Protocatechuic aldehyde was not actually detected among the products, but protocatechuic acid and pyrocatechin were found (Tiemann & Haarmann).

**VETCH.** *Vicia sativa*.—The composition of three varieties of vetch-seed has been determined by H. Weiske-Proskau (*Ann. d. Landwirthschaft. Wochenblatt*, Sept. 6, 1871; *Chem. Soc. J.* [2], x. 840).

	Ordinary	White	Grey
Water . . . . .	12.93	13.68	14.36
Proteids . . . . .	27.50	27.81	29.06
Soluble Carbo-hydrates and Fats . . . . .	47.80	48.03	46.72
Crude Fibre . . . . .	7.17	6.87	6.22
Ash . . . . .	4.60	3.61	3.64
	100	100	100

On the formation of Asparagin in vetches, see p. 108.

**VINYL-COMPOUNDS** (E. Baumann, *Ann. Ch. Pharm.* cxliii. 308). The *bromide* and *iodide* of vinyl,  $C^2H^3Br$ , and  $C^2H^3I$ , are acted on by *sodium methylate* at ordinary temperatures, even in the shade, yielding the same products as when the action takes place at a higher temperature, viz. acetylene, sodium bromide, methyl alcohol, and a trace of a substance which may perhaps be allyl alcohol, as it gives rise to an odour exactly resembling that of acrolein when treated with dilute sulphuric acid and potassium dichromate.

Pure *potassium cyanide* (prepared by saturating alcoholic potash with gaseous hydrocyanic acid) and *silver cyanide*, have practically no action on vinyl bromide, even after several hours' heating at  $140^\circ$ – $150^\circ$ .

When vinyl bromide is kept in a sealed tube in the dark, no change ensues, even after several weeks; but if exposed to direct sunlight, it becomes changed into an isomeric, solid, non-crystalline, porcelain-like, elastic substance; this change takes place more rapidly with moist bromide than with the perfectly dry substance; the presence of a small quantity of alcohol neither accelerates nor retards the change. This solid substance has the sp. gr. 2.075, whereas the liquid bromide has the sp. gr. 1.62 (Regnault). It begins to decompose at  $125^\circ$ – $130^\circ$ , and is but little acted on by boiling alcoholic potash; after twelve hours heating to  $180^\circ$ – $200^\circ$ , with this reagent, however, it forms a brown-black substance, insoluble in all menstrua, all the bromine being removed from it without evolution of gas. Sulphuric acid carbonises the substance on being heated with it; boiling nitric acid has but little action on it; bromine dissolves it, forming a loose compound, which splits up into bromine and the original substance, on treatment with water, alcohol, or alkalis.

Vinyl chloride undergoes a change by the action of sunlight, producing an isomeride of similar appearance and properties to the above-described substance. The specific gravity of the solid modification is 1.466; it can be heated to  $120^\circ$  without decomposition, but melts to a black-brown mass at a higher temperature, it is not dissolved by bromine.

Dichlorethylidene (chlorinated vinyl chloride), boiling at  $86^{\circ}$ , is also changed into a solid isomeride by the action of light. This body has been described by Regnault, and a similar modification of brominated vinyl bromide by Sawitsch.

The preparation of vinyl iodide from ethylene iodide is difficult, the yield being very small; it is not obtained by the action of potassium iodide on vinyl bromide; sunlight decomposes it, setting free iodine, which probably prevents the isomeric transformation of the unaltered iodide, as a trace of free iodine prevents this change in the case of vinyl bromide.

**VIRIDINE**,  $C^{12}H^{10}N$ . On the occurrence of this base in tobacco-smoke, *see* TOBACCO (p. 1161).

**VIVIANITE**,  $3FeO.P^{20}_2 + 8H^2O$ , or  $Fe^2(PO^4)^2 + 8H^2O$ . Maskelyne & Flight (*Chem. Soc. J.* [2], ix. 6) have analysed several specimens of vivianite from Cornwall.

*a.* Pale blue-green crystals (examined crystallographically by G. vom Rath, *Pogg. Ann.* cxxvi. 405), occurring with quartz, and chalybite in the cavities of a gangue composed of blende, with small quantities of galena, iron pyrites, copper pyrites and mispickel. *b.* From the same locality; dark blue fragments of pulverulent structure, sometimes enclosing imperfect dark brown crystals. *c.* and *d.* Fine crystals from Fernando Po.

	FeO	FeO*	P <sup>20</sup> O*	CO*	SiO*	H <sup>2</sup> O	Organic matter	
<i>a.</i>	42.71	1.13	28.53	—	—	28.98	—	101.33
<i>b.</i>	37.21	9.17	23.90	5.16	0.81	23.87	0.29	100.41
<i>c.</i>	42.89	0.80	28.79	—	—	29.44	—	101.92
<i>d.</i>	38.50	5.08	27.80	—	—	28.33	—	99.71

The whole of the iron was doubtless originally present as monoxide; but the nearly colourless powder of the variety *a* oxidises even during trituration, its colour changing to deep blue. Bearing this in mind, the composition of all the species may be represented by the ordinary formula of vivianite.

**VOLCANIC EMANATIONS.** On the Gases evolved from the Fumaroles of Vesuvius and Etna, *see* Scacchi (*Min. Mitth.* 1871, 54; *Jahresb. f. Chem.* 1871, 1220; 1872, 1175).

On the Gaseous Exhalations from the Solfataras of Pozzuoli: S. de Luca (*Ann. Chim. Phys.* [4], xxvi. 289; *Jahresb.* 1872, 1175; *Chem. Soc. J.* [2], x. 294). *See* further the article GASES, VOLCANIC, in this volume (p. 550).

## W

**WAD.** C. P. Williams (*Chem. News*, xxi. 237) describes an anhydrous wad occurring in the quartz-veins of the gold districts of Nueva Providencia, Venezuela, containing: 46.973 p.c. MnO, 7.645 O, 4.073 Fe<sup>2</sup>O<sup>3</sup>, 15.934 Al<sup>2</sup>O<sup>3</sup>, 0.528 CuO, 3.555 CoO, 10.885 NiO, trace of ZnO, 1.605 CaO, 1.653 MgO, and 8.653 SiO<sup>2</sup>.

Analysis of three specimens of wad from different localities in Germany are given by H. Ludwig (*Arch. Pharm.* [2], cxliii. 101; *Jahresb.* 1871, 1284).

**WALNUT.** *See* RESININ (p. 1039).

**WATER.** On the Compressibility of Water, *see* LIQUIDS (p. 756).

*Specific Heat.*—G. A. Hirn finds that the specific heat of water does not exhibit any irregularity near its point of maximum density, but merely changes somewhat more quickly below than above that point (*Compt. rend.* lxx. 831).

*Freezing.*—Boussingault (*Compt. rend.* lxxiii. 77) observed that water enclosed at  $4^{\circ}$  in a cast-steel tube, thick enough to be regarded as inextensible, remained liquid for several days at  $-24^{\circ}$ , as was shown by the mobility of a steel ball enclosed within the tube. Solidification took place as soon as the tube was opened and the water allowed to expand.

Martins & Chancel (*Ann. Chim. Phys.* [4], xxvi. 560) have examined the physical phenomena attending the bursting of shells by the freezing of water. However low the temperature of the air might be, that of the enclosed water, at the moment of splitting of the shell, which took place without any scattering of fragments, never sank below  $-4.2^{\circ}$ . The proportion of water frozen varied from 20 to 30 p.c., and

the pressure thereby exerted was sufficient to reduce the entire volume by  $\frac{1}{15}$  to  $\frac{1}{10}$  (compare iii. 79).

According to Tellier (*Compt. rend.* lxxv. 506), ordinary water can be cooled in a glass vessel to  $-3^{\circ}$  or  $-4^{\circ}$  without freezing, even when briskly shaken. A very violent concussion, however, frequently causes it to freeze, and the solidification may be instantly determined by dropping in a crystal of ice, needless of ice being then formed, which traverse the entire mass, and the temperature rising to  $0^{\circ}$ . Those phenomena are similar to those which take place in supersaturated saline solutions.

Zöppritz (*Pogg. Ann. Ergänz.* v. 497) has shown by careful experiments that sea-water in freezing exhibits no deviation from the general law which governs the variation of density with temperature in all liquids excepting pure water.

Bolley (*Dingl. pol. J.* cxviii. 267) has shown that the concentration which is observed in sea-water and in strong saline solutions in general by the act of freezing, takes place also in spring and river-waters, even in such as have but a very slight degree of hardness. A litre of filtered water from the Lake of Zürich left on evaporation 0.128 gram of saline residue (dried at  $110^{\circ}$ ), whereas a litre of filtered water from the thawed ice of the same lake yielded only 0.026 gram.

**Decomposition.**—On the decomposition of water by zinc in conjunction with a more negative metal, see ELECTROLYSIS (p. 454).

H. T. Brown (*Chem. Soc. J.* [2], x. 577) finds that water is decomposed during vinous fermentation, and that the decomposition is facilitated by an increase of atmospheric pressure.

According to V. Meyer (*Compt. rend.* lxxiv. 195), vapour of water passed over boiling sulphur is decomposed, with formation of sulphurous and thiosulphuric acids.

**Detection and Estimation.**—For the detection of water in the state of vapour Schorax (*Deut. Chem. Ges. Ber.* iii. 11) recommends paper impregnated with solution of calcium platinocyanide, and decolorised by heating. Exposure to vapour of water immediately restores the colour.

The presence of water in common Ether may be detected by dropping the ether into carbon sulphide previously purified by means of silver amalgam. The slightest quantity of water produces a milky turbidity (V. Wartha, *Deut. Chem. Ges. Ber.* iii. 82).

Water may be detected in *Essential Oils* by the turbidity which it produces when the oil is mixed with several times its volume of petroleum ether (Louché, *J. p. Chem.* [2], vi. 159).

On the estimation of water in *Acetic acid* by observation of the freezing temperature of the aqueous acid, see ACETIC ACID (p. 5).

On the mode of combination of *Water of Crystallisation*, see F. v. Kobell (*Pogg. Ann.* cxli. 446; *Jahresb. f. Chem.* 1870, 204).

F. Mohr infers from Landolt's tables of the boiling points, specific gravities, and refractive indices of isomeric bodies, that when hydrogen is present in a compound in the form of water, it lowers the index of refraction, but raises the specific gravity and the boiling point (*Deut. Chem. Ges. Ber.* iv. 156).

**Water Analysis. Estimation of free Oxygen.**—Schützenberger a. Gérardin (*Compt. rend.* lxxv. 879) estimate the free oxygen in water by means of sodium hyposulphite,  $\text{NaHSO}_3$  (Schützenberger's hydrosulphite, 1st *Suppl.* 1063), which absorbs oxygen with great rapidity. The reaction consists in the conversion of the hyposulphite into the acid sulphite of sodium, and the amount of hyposulphite thus oxidised by a water is determined by means of Couper's soluble aniline-blue, which is instantly decolorised by the hyposulphite, and not affected by the acid sulphite. Sodium hyposulphite also decolorises an ammoniacal solution of cupric oxide, while the sodium sulphites do not, and this solution may also be used as a means of titrating the test-solution of hyposulphite. It is necessary to exclude the air from the water during its treatment with the hyposulphite, and for this purpose it is covered with a thin layer of oil, beneath which the beak of the burette is made to dip. The hyposulphite solution is added from a burette, first to the standard solution of copper to determine its strength, and then to a litre of the water coloured with Couper's blue. The disappearance of the colour in each case shows the presence of anoxidised hyposulphite, and therefore the completion of the action.

A method of detecting air dissolved in water is described by A. Andersen (*Pogg. Ann.* cxliii. 142; *Jahresb. f. Chem.* 1871, 205).

On the estimation of *Carbonic acid* in Sea-water, see p. 261 of this volume; in Chloraous Spring-water; K. Knapp (*Ann. Ch. Pharm.* cxviii. 112; *Chem. Soc. J.* [2], ix. 482).

On the estimation of *Sulphuric acid* in water, see A. Müller (*Deut. Chem. Ges. Ber.* iii. 881; *Chem. Soc. J.* [2], ix. 439).

On the detection and estimation of *Nitrous* and *Nitric acid* in Waters, see pp. 854, 858. On the estimation of *Nitric acid*, see also Wittstein (*Dingl. pol. J.* cc. 123; *Chem. Soc. J.* [2], ix. 754). E. Nicholson (*Chem. News*. xxvi. 89); F. Schulze (*Zeitschr. anal. Chem.* 1872, 313; *Jahresb.* 1872, 881).

On the estimation of *Nitrates* in Well Water: J. M. Bemmelen (*Zeitschr. anal. Chem.* 1872, 136; *Jahresb.* 1872, 881).

On the estimation of *Ammonia* in Well and River Waters, see H. Fleck (*J. pr. Chem.* [2], v. 263; *Chem. Soc. J.* [2], x. 1041).

On the detection and estimation of *Organic matter* in Water, see A. Müller (*Deut. Chem. Ges. Ber.* iii. 659; *Jahresb. f. Chem.* 1870, 875); also Wittstein (*Dingl. pol. J.* cc. 123; *Chem. Soc. J.* [2], ix. 754), also E. Schürmann (*J. pr. Chem.* [2], iv. 374; *Jahresb. f. Chem.* 1871, 876). On Frankland's method of estimation: *Chem. News*, xxv. 157.

On the determination of *Nitrogenous Organic matter*, see J. A. Wanklyn (*Chem. News*, xxiv. 10; xxv. 157); D. Campbell (*ibid.* xxiv. 19).

On the determination of the quality of *Potable Waters*, see Almén (*Deut. Chem. Ges. Ber.* iv. 750); also G. Bischof (*Zeitschr. anal. Chem.* x. 441). This paper contains descriptions and figures of the microscopic appearances presented by the evaporated residues of potable waters contaminated with various kinds of organic matter.

On the alterations of *Potable Waters*, see J. Müller (*Arch. Pharm.* [2], cxlix. 27; [3], i. 385; *Jahresb. f. Chem.* 1871, 165).

Determination of the *Hardness of Waters*: E. Reichardt (*Zeitschr. anal. Chem.* 1871, 284); A. Wagner (*Arch. Pharm.* [2], cl. 235); Gröger (*N. Jahrb. Pharm.* xxxvi. 1; *Jahresb. f. Chem.* 1872, 877); of the *Temporary Hardness*: A. Wagner (*Dingl. pol. J.* cci. 426; *Chem. Soc. J.* [2], x. 23).

For analyses of *Sea Water*, see *Jahresb. f. Chem.* 1870, 1380; 1871, 1222: of *Lake and River Water*, *ibid.* 1871, 1223; 1872, 1180: of *Spring and Mineral Waters*, *ibid.* 1870, 1382-1391; 1871, 1225-1233; 1872, 1181-1188.

On the composition of *Drainage Water*, see Voelcker (*Chem. Soc. J.* [2], ix. 276-297).

On the composition of *Water for feeding Steam-Boilers*, and the methods of *Softening* it, see J. Stingl (*Dingl. pol. J.* cvi. 304; *Jahresb. f. Chem.* 1872, 970).

**WATER-GLASS.** According to Flückiger (*Arch. Pharm.* [2], cxliv. 97; *Jahresb. f. Chem.* 1870, 305) the precipitate formed in solutions of water-glass by very soluble salts of potash, soda, lithia, and ammonia, consists of silica. Reintz, on the other hand (*Deut. Chem. Ges. Ber.* iv. 104) finds that soda water-glass gives with strong aqueous ammonia a precipitate containing soda and silica in the ratio  $\text{Na}_2\text{O} : 4\text{SiO}_2$ . The precipitate formed by a strong solution of sodium nitrate has the composition  $\text{Na}_2\text{SiO}_3 + 8\text{H}_2\text{O}$ . Water-glass behaves therefore with neutral salts of potassium and sodium just like soaps, excepting that the latter are precipitated by caustic potash, whereas in the water-glass solution the precipitate is produced only by ammonia. This circumstance may be made available for the preparation of perfectly pure water-glass.

On the use of *Gates* (p. 536) for the preparation of water-glass, see Scheurer-Kestner (*Compt. rend.* lxxi. 767; *Chem. Soc. J.* [2], ix. 783).

**WAVELLITE.** This mineral occurs as a thin coating on the cleavage-faces of amblygonite (p. 972), forming small radiate spherules, the needles of which have the form of strongly-striated prisms. An analysis by Pisani gave:

F	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	
2.27	84.30	38.26	26.60	= 101.42 Sp. gr. = 2.33.

(Des Cloizeaux, *Compt. rend.* lxxv. 69).

**WAX.** On the formation of Bees-wax, and the proportion of wax in Pollen, see **POLLEN** (p. 1006).

**Straw-wax.**—J. König (*Deut. Chem. Ges. Ber.* iii. 566) confirms the observations of Radziejewski respecting the occurrence of wax in the straw of cereals (*1st Suppl.* 1128), and adds that it is also contained in meadow and clover hay and in pea straw. In meadow and clover hay he found 1.0 to 1.3 p.c. true fat, together with 0.4 to 0.6 p.c. wax; rye and barley-straw yielded about 0.5 p.c. fat, and the same quantity of wax. See **FAT** (pp. 506, 507).

**WEBSTERITE** or **ALUMINITE.** This mineral has been found in the chalk near Brighton, forming a layer about 3 feet thick, and probably filling a cleft; above

It is a ferruginous clay with nodules of limonite, flint, and isolated crystals of gypsum. The websterite is of very variable constitution, sometimes in the form of the finest white powder, appearing under the microscope as an aggregate of extremely fine crystals, sometimes in compact nodular masses resembling meerschaum (S. Percival, *Jahrbuch. f. Mineralogie*, 1871, 637).

**WINE. Preservation.**—To preserve wine in good condition. Pasteur (*Bull. Soc. Chim.* [2], iv. 80, 410) recommends that it be heated for some minutes in perfectly filled and tightly corked bottles, or in casks, to 60°–70° (perhaps even 45° would be high enough), in order to destroy the vitality of the cryptogamic germs, which are the cause of its deterioration. Wine thus heated is quite clear after cooling, undergoes no alteration in colour, taste, or odour, and keeps well even in half-filled bottles.

An apparatus for carrying out this process on the large scale has been constructed by Giret a. Vinas (*Dingl. pol. J.* cci. 550). It consists of two upright cylinders of tinned copper, one serving as a heating vessel, and the other as a cooler, in which the wine circulates through annular jackets of the same height as the cylinders. The wine first passes through the cooler, then passes into the heating apparatus, where it traverses the annular jacket—which is warmed externally by water to 55°–60°—thence it passes into the annular jacket of the cooler, and finally leaves the apparatus. It is essential that the wine be not heated above 60°, otherwise it acquires a boiled taste, and that the apparatus be perfectly closed to prevent the escape of any of the volatile odoriferous principles of the wine.

A table of the composition of German and other wines is given by G. Glässner (*Arch. Pharm.* [2], cxlix. 117; *Jahresb. f. Chem.* 1872, 1043).

**Analysis of Wine.** On the Spectroscopic examination of Wine, and its application to the detection of Adulteration, see Sorby (*Quar. Jour. of Microscopical Science*, 1869, 358; *Jahresb. f. Chem.* 931).

On methods of distinguishing between Grape and Fruit wines (made from apples, pears, gooseberries, currants, &c.), see *Zeitschr. anal. Chem.* 1871, 231; 1872, 337; *Jahresb.* 1871, 967; 1872, 936.

On the Detection of the addition of Spirit to Wine (so-called *gallisation*), see Schubert (*Zeitschr. anal. Chem.* 1870, 112; *Jahresb.* 1870, 1043).

**Estimation of Free Acid.**—F. Schwachhöfer (*Zeitschr. anal. Chem.* 1872, 331) estimates the quantity of free acid in red wine by mixing the wine with tincture of litmus, supersaturating with caustic baryta, and titrating back with sulphuric acid. As the point of saturation is approached, every drop of sulphuric acid added produces a red zone. For the titration 10 c.c. of wine are used; 1 c.c. baryta-solution = 0.009852 gram of tartaric acid (eq. 75), and 1 c.c. sulphuric acid = 16 c.c. of baryta-solution.

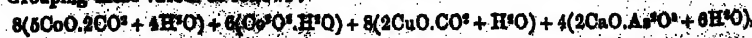
**Estimation of Cream of Tartar in Wine.**—P. Carles recommends for this estimation, in place of the old method of incineration, which is not exact, the process devised by Berthelot a. Fleuriou, which consists in precipitating the acid tartrate of potassium by adding to the wine an equal volume of a mixture of alcohol and ether, washing the crystalline precipitate slightly with alcohol, redissolving it in water, and estimating the tartaric acid by titration with a standard alkaline solution (*J. Pharm. Chim.* [4], xiv. 188; *Chem. Soc. J.* [2], ix. 1211).

**Estimation of Sugar in Wine** (Schubert, *Zeitschr. anal. Chem.* 1870, 112; *Jahresb. f. Chem.* 1870, 1037).

**WINKLERITE** (Breithaupt, *Jahrb. f. Mineralogie*, 1872, 816). An amorphous bluish-black to velvet-black mineral from Oria near Matril in the Sierra Almahilla, Spain, also found on the Rothenberg near Saalfeld. Hardness = 3. Sp. gr. = 3.432. An analysis by C. Winkler gave the values A, together with potash and soda, recognisable by the spectroscope. Deducting  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  as admixtures, and reckoning the nickel with the cobalt, we obtain the values B, which Winkler represents by the formula:



Grouping these values as follows:



the whole may be regarded as an intimate mixture of malachite, pharosolite, cobaltic hydrate, and cobaltous carbonate. The mineral may have been formed by the action of calcareous water containing carbonic acid on cobalt-bloom in contact with malachite.

	CoO	NiO	CaO	FeO	Fe <sup>2</sup> O <sup>3</sup>	CaO	As <sup>2</sup> O <sup>3</sup>	CO <sup>2</sup>	SiO <sup>2</sup>	H <sup>2</sup> O
A.	22.91	2.38	12.31	10.24	8.05	6.85	10.22	10.87	2.64	14.06 = 100.63
B.	33.10	—	13.89	10.88	—	5.92	10.55	10.99	—	14.80 = 100
C.	33.17	—	14.11	11.20	—	4.97	10.23	11.73	—	14.06 = 100

**WINKWORTHITE** (H. How, *Phil. Mag.* [4], xli. 270). A mineral occurring in colourless transparent nodules, some as big as a nut, in the gypsum of Winkworth, Hants County, Nova Scotia. The numbers in the two following analyses are intermediate between those required by the formulæ:

$11\text{CaO}, \text{SiO}_2, 9\text{SO}_3, 3\text{B}_2\text{O}_3, 20\text{H}_2\text{O}$ , and  $11\text{CaO}, \text{SiO}_2, 8\text{SO}_3, 4\text{B}_2\text{O}_3, 20\text{H}_2\text{O}$ :

CaO	SO <sub>3</sub>	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub> *	H <sub>2</sub> O
31.66	36.10	3.31	10.13	18.80 = 100
31.14	31.51	4.08	14.37	18.00 = 100

\* Determined by loss.

Kenngott (*Jahrb. f. Mineralogie*, 1872, 300) shows by calculation that these formations are mixtures of silico-boracalcite, 77.87 p.c., and gypsum, 67.75 p.c.

**WINTERGREEN OIL.** According to J. Broughton (*Pharm. J. Trans.* [3], ii. 281) the oil of *Andromeda Leschenaultii* consists of methyl-salicylic acid, and is nearly identical with Canadian wintergreen oil.

**WOOLMINITE.** See BAUXITE (p. 126).

**WOHLERITE.** See TANTALATES (p. 1146).

**WOLLASTONITE.** G. vom Rath (*Jahresb. f. Mineralogie*, 1872, 217) describes an outcast from Monte Somma, consisting of a nucleus of compact limestone surrounded by a shell of wollastonite arranged in layers perpendicular to the circumference. Between the shell and the nucleus there is a zone of limestone not sharply defined on its inner surface, rich in wollastonite fibres (58.49 p.c. wollastonite) whilst the central mass contains only 25.33 p.c. of silicate. There is here abundant evidence of a metamorphism, proceeding from without inwards, of carbonate into silicate. An analysis of the wollastonite (sp. gr. = 2.853) gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Loss by ignition
51.31	1.37	45.66	0.73	0.75 = 90.82.

**WOOD.** On the Distillation of Wood, see Watson Smith (*Chem. Soc. J.* [2], ix. 1101).

**WOOL.** On the Action of Alkalis upon Wool, see LANUGINIC ACID (p. 723), and SERICIC ACID (p. 1080).

A method of distinguishing between wool and silk, founded on the presence of sulphur in wool, is given by E. Kopp (*Moniteur Scientifique*, [3], i. 683). The (white) sample to be tested for wool is immersed in a solution of lead oxide in potash-ley, whereupon, if wool is present, black lead sulphide will be produced. See further, *Dingl. pol. J.* ccc. 563; *Chem. News*, xxvi. 100.

On the Composition of Sheep's Wool, and on the Extraction of Fat-acids together with Wool-grease from the Soap-waters of Wool-washing, see Märker a. Schulze (*J. pr. Chem.*, cviii. 193; *Jahresb. f. Chem.* 1870, 811; *Dingl. pol. J.* cxcv. 173; cxvii. 571; *Jahresb. f. Chem.* 1869, 811; 1870, 1232).

The process of washing and dyeing wool, devised by Ensom a. Spence, is described by C. Bollé (*Dingl. pol. J.* cci. 435; *Jahresb.* 1871, 1104).

On Dyeing Woollen Cloth with Amarant-colour, see Pfundheller (*Dingl.* cci. 179; *Jahresb.* 1871, 1100); with Scarlet, B. Jegel (*Dingl.* cciii. 422; *Jahresb.* 1872, 1072).

**Wool-grease.**—On the Composition of the Grease (*suint*) from Sheep's Wool, see CHOLESTERIN (p. 330).

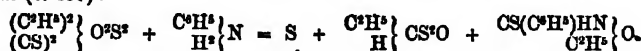
The substance there mentioned as separating in white-flocks from solution in alcohol has since been shown by Schulze to be an isomeric of cholesterol (*J. pr. Chem.* [2], vii. 163; *Chem. Soc. J.* [2], xi. 1219).

**WORMWOOD OIL.** On the Index of Refraction of this oil, see LIGHT (p. 740).

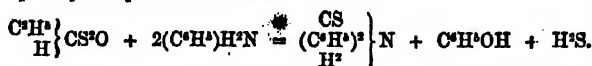
**WULFENITE.** On Chromo-wulfenites, see Schauf (*Proc. Roy. Soc.* 1871, 461; *Chem. Soc. J.* [2], ix. 601).

## X

**XANTHAMIDE.** Phenyl-xanthamide,  $\text{CS}(\text{C}^6\text{H}_5)\text{HN}(\text{C}^6\text{H}_5)$  O, is formed, together with xanthic acid and free sulphur, by the action of aniline on ethyldisulphocarbonic sulphide (v. 499):



A portion of the xanthic acid is further acted upon by the excess of aniline present, forming diphenylsulphocarbamide:



Phenyl-xanthamide forms triclinic crystals, more soluble in alcohol than sulphocarbamide (A. W. Hofmann, *Deut. Chem. Ges. Ber.* iii. 172).

**XANTHINE.** This substance has been found by G. Lebon (*Compt. rend.* lxxiii. 47) in a urinary calculus consisting of a superficial layer 1 mm. thick of calcium phosphate mixed with ammonium-magnesium phosphate, an equally thin layer of calcium oxalate, and a nucleus, forming the greater part of the stone, consisting of xanthine with a small quantity of calcium urate.

**XANTHOCOBALE COMPOUNDS.** See COBALT (p. 364).

**XANTHOPHYLLITE.** In the xanthophyllite of the Schischimskian mountains near Slatoust, Jeremejew has observed microscopic diamonds of varying size irregularly distributed through the plates of the mineral (*Jahresh. f. Mineralogie*, 1871, 276; *Chem. Soc. J.* [2], ix. 667). In connection with these observations Jeremejew has collated some of the older statements regarding xanthophyllite, from which it appears that this mineral occurs not only of yellow shades, but also colourless, brownish, light gray and yellowish green. Hardness = 5. Sp. gr. = 3.035 – 3.062. Optically uniaxial.

A. Knop (*Jahresh. f. Mineralogie*, 1872, 785) has published several analyses of xanthophyllite by G. Wagner (a), O. Schifferdecker (b), and himself (c. and d). On account of the great variations in the amount of water (two other specimens gave 2.33 and 3.83 p.c.), Knop regards it as unessential, and assigns to xanthophyllite the formula  $2(\text{RO}.\text{SiO}_2) + 3(\text{RO}.\text{R}'\text{O})$ .

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{H}_2\text{O}$
17.42	44.18	3.53	11.95	20.61	2.61 = 100.80
17.7	43.6	2.9	11.5	20.9	2.5 = 99.1
16.38	undet.	3.00	11.49	undet.	1.35
16.04	"	2.10	11.50	"	2.08

**XYLENE.**  $\text{C}^6\text{H}_{10} = \text{C}^6\text{H}(\text{CH}_3)_2$ . On the Xylenes and Cumenes of Coal-tar, see CUMENE (p. 402).

*Orthoxylene* is produced by heating liquid bromotoluene, dissolved in pure benzene, with methyl iodide and sodium. The product, purified by fractional distillation, boils at  $141^\circ$ – $143^\circ$  (the column of mercury being wholly in the vapour), has a faint and agreeable aromatic odour, and does not solidify at  $-22^\circ$ . By oxidation with dilute nitric acid, it yields paratoluic acid (m. p.  $178^\circ$ ) and orthotoluic acid (m. p.  $104^\circ$ – $106^\circ$ ), in the proportion of about 1 to 3. With fuming nitric acid either in the cold or at boiling heat, it yields only liquid compounds, from which after some weeks a few crystals separate (Jannasch & Häbner, *Zeitschr. f. Chem* [2], vii. 706).

*Isoxylene* or *Metaxylene*.—This modification may be obtained nearly pure by heating commercial xylene (which is a mixture of isoxylene and methyl-toluene or paraxylene) with dilute nitric acid, the methyl-toluene being thereby oxidised, while the isoxylene remains unattacked. From this isoxylene, *dinitro-isoxylene*, and *ammonio-nitroisoxylene* or *nitroxylene* (1st Suppl. 294, 1181) were prepared. The latter yields, through the medium of the diazo-compound, a  $\beta$ -nitroxylene  $\text{C}_6\text{H}_3(\text{NO})_2$ , which solidifies at low temperatures, melts at  $+2^\circ$ , boils at  $237^\circ$ – $239^\circ$ , and has a sp. gr. of 1.126 at  $17.6^\circ$ . By oxidation with chromic acid it is converted into nitro-toluic acid (1st Suppl. 1195). By reduction it yields *p*-xylylene (p. 1205).



**Chloroxylenes.** *Monochloroxylene*, or *Xylol Chloride*,  $C^6H^4 \begin{Bmatrix} OH \\ CH^2Cl \end{Bmatrix}$ , is produced by the action of chlorine on coal-tar xylene. When heated with water to  $200^\circ$  in sealed tubes, it splits up into dimethyl-anthracene,  $C^{10}H^{14} = C^4H^4(C^2H^5)^2$ , xylol-xylene,  $C^8H^{10} = C^6H^4(C^2H^5)$ , and hydrochloric acid:



See ANTHRACENE (p. 84).

*Dichloroxylene*, or *Xylylene Chloride*,  $C^6H^4Cl^2 = C^6H^4 \begin{Bmatrix} CH^2Cl \\ CH^2Cl \end{Bmatrix}$  (called *tollylene chloride* by Grimaux), is produced by the action of chlorine at  $140^\circ$  on methyl-toluene (paraxylene), (Grimaux, *Compt. rend.* lxx. 1363). It may also be obtained by the action of chlorine on commercial xylene at the boiling heat, though less advantageously, as commercial xylene contains but a small proportion of methyl-toluene (v. 1057).

Dichloroxylene oxidised by chromic acid mixture is converted into terephthalic acid. Heated with water to  $170^\circ$ – $180^\circ$  it is resolved into hydrochloric acid and dihydroxyl-xylene or xylylene glycol,  $C^6H^4(OH)^2$ . Heated with sodium acetate, it yields the monoacetate and diacetate of xylylene, and with sodium benzoate, the monobenzoate of xylylene.

*Dibromoxylene* or *Xylylene Bromide*,  $C^6H^4Br^2 = C^6H^4(CH^2Br)^2$ , is prepared by dropping into boiling methyl-toluene  $2\frac{1}{2}$  times its volume of bromine, washing the cooled mass with ether, and recrystallising from alcohol. It is also formed by distilling xylylene glycol with hydrobromic acid. It dissolves sparingly in ether, easily in chloroform, and crystallises therefrom in rhombic laminae which melt at  $145^\circ$ – $147^\circ$ .

*Di-iodoxylene*, or *Xylylene Iodide*,  $C^6H^4(CH^2I)^2$ , is obtained by boiling xylylene glycol for a few minutes with strong hydriodic acid (b. p.  $127^\circ$ ). It forms slender needles, slightly soluble in ether, easily soluble in boiling alcohol and in chloroform. It quickly turns yellow when exposed to the air, melts and becomes coloured at about  $170^\circ$ , and decomposes at a higher temperature.

*Dihydroxyl-xylene*, or *Xylylene-glycol*,  $C^6H^4 \begin{Bmatrix} CH^2OH \\ CH^2OH \end{Bmatrix}$ , is prepared by heating the chlorine or bromine compound with 30 times its weight of water to  $170^\circ$ – $180^\circ$ , concentrating the aqueous solution, neutralising with alkaline carbonate, and extracting the glycol with ether. It crystallises from ether in shining needles, dissolves easily in water, alcohol and ether; melts at  $112^\circ$ – $113^\circ$ . With chlorine, bromine, or iodine, it yields the chloride, bromide, or iodide of xylylene. By sulphuric acid and potassium dichromate it is oxidised to terephthalic acid.

*Condensed Glycols* appear to be formed by heating xylylene chloride or bromide with water to  $200^\circ$ . They are yellow masses insoluble in all menstrua.

*Monobenzoxy-xylene*, or *Xylylenemonobenzoate*,  $C^6H^4 \begin{Bmatrix} OH \\ OC^6H^5O \end{Bmatrix}$ , obtained by heating the dichloride with an alcoholic solution of sodium benzoate, forms long thin needles which melt at  $73^\circ$ – $74^\circ$ , and dissolve readily in alcohol and in ether.

*Diacetoxyl-xylene*, or *Xylylene diacetate*,  $C^6H^4(OC^2H^5O)^2$ , obtained by heating the dichloride with alcoholic sodium acetate to  $150^\circ$ , crystallises in hard shining laminae, having a hot camphorous taste, easily soluble in alcohol and ether. By distillation it appears to yield the monoacetate (Grimaux).

**XYLIDINE**,  $C^6H^4N = C^6H^4NH^2 = C^6H^4(NH^2) \begin{Bmatrix} CH^2 \\ CH^2 \end{Bmatrix}$ . Hofmann & Martius (*Deut. Chem. Ges. Ber.* ii. 411) have obtained from commercial aniline oil, by fractional distillation, a xylidine boiling constantly at  $212^\circ$ . This xylidine does not yield colouring matters by oxidation, either alone or when mixed with toluidine, but when mixed with pure aniline it yields by the ordinary treatment a colouring matter resembling rosaniline (Hofmann, *ibid.* 378).

By nitrating synthetically prepared ethylbenzene, and reducing the nitro-compound with tin and hydrochloric acid, a xylidine was obtained, likewise boiling at  $212^\circ$  but nevertheless not identical with the xylidine above mentioned; it smells like aniline prepared from indigo, its salts are more soluble, and it does not yield colouring matters by oxidation either alone or with toluidine or aniline (Hofmann).

Tavildarow (*Deut. Chem. Ges. Ber.* ii. 558; *Zeitschr. f. Chem.* vi. 418) has prepared xylidine (distinguished as  $\beta$ ) from coal-tar xylene (purified by prolonged boiling with dilute nitric acid), by nitration and reduction with tin and hydrochloric acid. The xylidine, separated by potash, was obtained as a colourless liquid, having a sp. gr. of

0.985 at 18.5°, and boiling at 216°; 100 pts. water at 18° dissolve 3.319 pts. of it. The *oxalate* crystallises well and dissolves to the amount of 3.846 pts. in 100 pts. water at 21.5°. The *acetyl-derivative* crystallises in needles and melts at 128°.

The crude xylidine, when distilled, yielded between 235° and 246°, a solid body melting at 89°, which gave with hydrochloric acid a compound having the composition  $(C^8H^7Cl)^2N.HCl$  (Tawildarow).

*Bromoxylidine*,  $C^8H^7Br.NH^2$ , is formed from acetobromoxylide,  $C^8H^7Br.NH(C^2H^3O)$  (1st Suppl. 1131), by distillation with soda-ley. Should it be contaminated with dibromoxylidine, it must be dissolved in hydrochloric acid, the solution evaporated to dryness, the monobromoxylidine hydrochloride dissolved out by hot water, and the free base precipitated by ammonia. Bromoxylidine is insoluble in cold, and but slightly soluble in hot water. It dissolves easily in alcohol and ether, and crystallises from dilute alcohol in white microscopic needles melting at 96°-97°. The *hydrochloride* forms white needles; its aqueous solution forms with platinic chloride a light yellow crystalline precipitate (Genz, *Deut. Chem. Ges. Ber.* iii. 226).

*Acetodibromoxylide* is formed by agitating acetoxylyde with the calculated quantity of bromine-water. It is insoluble in water, and crystallises from alcohol in white shining crystals (Genz).

*Dibromoxylidine*,  $C^8H^7Br^2.NH^2$ , produced by distilling aceto-dibromoxylide with potash-ley, crystallises from alcohol in needles. Its hydrochloride gives off hydrochloric acid when boiled with water (Genz).

*Phenylxylidine*,  $C^8H^7.NH(C^6H^5)$ , is produced by heating xylidine with aniline hydrochloride. It melts at 52°, boils at 278°-282° under a pressure of 485 mm. and at 173° under 15 mm. Soluble in alcohol, ether, benzene, and light petroleum oil. The *hydrochloride* is best obtained by passing hydrochloric acid gas into a solution of the base in benzene (Girard a. Vogt, *Bull. Soc. Chim.* [2] xviii. 67).

*Tolylxylidine*,  $C^8H^7.NH(C^7H^7)$ , crystallises from alcoholic solution in long, white, silky, light needles melting at 70°. It boils at 194° in a vacuum, and at 298°-300° under a pressure of 487 mm. (Girard a. Vogt).

*Diacylidine*,  $(C^8H^7)^2HN$ , obtained by heating xylidine with its hydrochloride, is a mixture of isomeric bodies, one of which is liquid, while the other is crystalline and melts at 162° (Girard a. Vogt).

*Naphthylxylidine*,  $C^8H^7.NH(C^{10}H^7)$ , obtained by heating xylidine hydrochloride with naphthylamine, is a thick liquid quickly turning brown and boiling at 243°-246° under a pressure of 15 mm. (Girard a. Vogt).

**XYLYL-CARBAMIDE**, or **XYLYL-UREA**,  $N^2H^4(CO)C^8H^7$ , is produced on mixing a solution of xylidine sulphate with potassium cyanate. After washing with warm water and recrystallisation from alcohol, it forms white needles melting at 186° (Genz).

*Diacylylcarbamide*,  $N^2H^4(CO)(C^8H^7)^2$ , formed by heating urea with three times its weight of xylidine, is insoluble in water, slightly soluble in boiling alcohol, ether, benzene, chloroform, and acetic acid, and crystallises from hot alcohol in snow-white felted needles, which do not melt at 250° (Genz).

**XYLYL-CARBIMIDE**, or **XYLYL ISOCYANATE**,  $N(CO)^2(C^8H^7)$ . See CYANIC ETHERS (p. 407).

**XYLYL-GUANIDINE (DI-)**,  $C(C^8H^7)^2H^2N^2$ , formed by the action of dry cyanogen chloride on xylidine, forms large white plates sparingly soluble in cold, more easily in hot water, very soluble in alcohol and ether. Its *platinichloride* has the composition  $2[C(C^8H^7)^2H^2N^2.HCl].PtCl^4$ . A base having the same composition is formed by the mutual action of sulphocarbonyl, alcoholic ammonia, and lead oxide (Genz).

**XYLYLENE ALCOHOL and ETHERS.** See XYLENE (p. 1209).

**XYLYL-NAPHTHYLAMINE.** See NAPHTHYL-XYLIDINE, *See (supra)*.

**XYLYL-URETHANE**,  $CO \begin{Bmatrix} NH.C^8H^7 \\ OC^8H^7 \end{Bmatrix}$ . See CARBAMATES (p. 263).

**XYLYL-XYLENE**,  $C^8H^7(C^8H^7)$ , is formed, together with dimethylxylidine, by heating xylid chloride with water in a sealed tube. See ANTHRACENE (p. 1208).

## Y

**YEAST.** See FERMENTATION (p. 516).

**YTTRIUM** and **ERBIUM** (Cleve & Hoeglund, *Bull. Soc. Chim.* [2], xviii. 193, 289). The oxides of these metals were prepared from gadolinite and separated from one another by the method of Bahr & Bunsen (v. 721).

The atomic weights of the metals, determined by the analysis of the sulphates, are  $Y = 50.7$ ;  $Er = 113.7$ . Bahr & Bunsen found  $Y = 61.7$ ;  $Er = 112.6$ .

An attempt to prepare the metals by electrolyzing the fused chlorides, or by reducing the chlorides by sodium, was only partially successful.

**Yttrium Salts.** These salts are colourless; their solutions do not give an absorption-spectrum, and they are, as a rule, less soluble than the corresponding salts of erbium. Both yttrium and erbium salts are precipitated by barium carbonate. The hydrate of yttrium is a white, gelatinous precipitate, obtained by the addition of a fixed alkali to a salt of yttrium. When calcined at a white heat, it is converted into yttrium oxide, a yellowish-white powder, very readily soluble in acids, even after ignition.

**Yttrium Chloride**,  $YCl_3 + 4H_2O$ , forms deliquescent prisms soluble in alcohol, insoluble in ether. When heated it loses hydrochloric acid, but the anhydrous chloride can be prepared by fusing together a mixture of hydrated chloride and sal-ammoniac.

The bromide,  $YBr_3 + 6H_2O$ , and the iodide closely resemble the chloride in appearance and solubility. The iodide is unstable, and rapidly becomes brown when exposed to the air.

**Fluoride**,  $YF_3$ .—Heavy, white, hygroscopic powder, but slightly soluble in dilute acids.

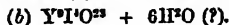
**Nitrate**,  $Y(NO_3)_3 + 4H_2O$ .—Occurs in large colourless crystals, easily soluble in water, alcohol, and ether. It is unalterable in the air, but loses 2 mols. of water when dried at  $100^\circ$ .

**Chlorate**,  $Y(ClO_3)_3 + 6H_2O$ .—The crystals of this salt are small colourless prisms, exceedingly deliquescent, soluble in alcohol, but very slightly so in ether.

**Perchlorate**,  $Y(ClO_4)_3 + 6H_2O$  (?).—Transparent crystals, very deliquescent, slightly soluble in alcohol.

**Bromate**,  $Y(BrO_3)_3 + 6H_2O$ .—Colourless needles, very soluble in water, slightly soluble in alcohol, almost insoluble in ether. It decomposes at  $100^\circ$ – $110^\circ$ . The iodate is a very definite salt, but not crystalline.

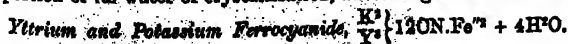
**Periodate**.—Two periodates are formed, according as the periodic acid employed in their preparation is in excess or not. The salt marked (a) is the most definite:



**Sulphate**,  $3Y_2SO_4 + 8H_2O$ .—Small transparent crystals, which lose their water of crystallisation at  $115^\circ$ . 100 pts. of water at  $15.5^\circ$  dissolve 9.3 pts. of crystallised, and 15.2 pts. of anhydrous sulphate; but on raising the temperature of the latter solution, a portion of the crystallised salt is deposited.

**Sulphocyanate**,  $Y(CNS)_3 + 4H_2O$ .—Well-defined prisms, soluble in water, alcohol, and ether, and permanent in the air.

**Platinosocyanide**,  $Y(CN)_3Pt + 7H_2O$ .—Like many platinosocyanides this salt crystallises in large, well-defined, dichroic crystals, red by transmitted light, and green or violet-blue by reflected light. It is easily soluble in water, but alcohol deprives it of a portion of its water of crystallisation, and changes its colour to a lemon-yellow.



**Double Sulphates**.—Two potassium salts were obtained, to which the formulae  $YK^+3SO_4$  and  $Y^+K^+3SO_4$  were assigned, but the analytical results did not agree very accurately with the calculated percentages. The sodium and ammonium salts were much more definite, and the formulae  $Y^+Na^+(SO_4)_2 + 2H^+O$  and  $Y^+(NH_4)^+(SO_4)_2 + 6H^+O$  may be regarded as correctly representing their composition.

The *sulphite*,  $\text{YSO}^3 + \text{H}^2\text{O}$ , is also a definite salt, crystallising in microscopic needles. It absorbs oxygen rapidly from the air.

*Selenate*,  $\text{YSeO}^4 + 3\text{H}^2\text{O}$  (?)—Large well-developed crystals, very soluble, and losing a portion of water of crystallisation in dry air.

*Selenite*,  $\text{Y}^2\text{H}^4(\text{SeO}^3)^4$ .—This salt occurs either as a white crystalline powder, or in the form of flattened microscopic prisms, according to the manner in which it has been prepared. It is soluble in mineral acids.

*Phosphates*.—The *metaphosphate*,  $\text{Y}(\text{PO}^3)^2$ , is a heavy crystalline powder insoluble in water and acids. The *pyrophosphate*,  $\text{Y}^2\text{H}^2.2\text{P}^2\text{O}^7 + 7\text{H}^2\text{O}$ , is a soluble salt; the *orthophosphate*,  $\text{Y}^2(\text{PO}^4)^3 + 4\text{H}^2\text{O}$ , is very sparingly soluble.

*Carbonate*,  $\text{YCO}^3 + \text{H}^2\text{O}$ .—Heavy white powder, indistinctly crystalline, and perfectly insoluble in water.

*Acetate*,  $2\text{Y}(\text{C}^2\text{H}^3\text{O}^2)^2 + 5\text{H}^2\text{O}$ .—Crystallises from its solution in colourless rhombohedrons, very soluble in warm water, but very sparingly in cold. It is permanent in the air.

*Oxalate*,  $\text{YC}^2\text{O}^4 + \text{H}^2\text{O}$ .—White crystalline powder, readily soluble in water acidulated with hydrochloric acid. It dissolves easily in concentrated solutions of potassium oxalate, forming the double salts,  $\text{Y}^2\text{K}^2(\text{C}^2\text{O}^4)^7 + 12\text{H}^2\text{O}$  and  $\text{Y}^2\text{K}^2(\text{C}^2\text{O}^4)^4 + \text{H}^2\text{O}$ .

*Double Carbonates*,  $\text{Y}^2\text{Na}^2(\text{CO}^3)^4 + 4\text{H}^2\text{O}$  and  $\text{Y}^2(\text{NH}^4)^2(\text{CO}^3)^4 + 3\text{H}^2\text{O}$ .

*Succinate*,  $\text{YC}^2\text{H}^3\text{O}^4 + x\text{H}^2\text{O}$  (?).

*Tartrate*,  $\text{Y}^2\text{H}^2(\text{C}^4\text{H}^3\text{O}^6)^4 + 6\text{H}^2\text{O}$ .—White crystalline precipitate, very slightly soluble in water.

**Erbium Salts.** These salts resemble those of yttrium in most of their properties. The only well-marked distinctive characteristics are the following.

The salts of erbium have a beautiful rose colour, and their solutions give absorption-bands. The appearance of their spectrum is quite different from that of didymium-salts. Erbium oxide dissolves with great difficulty, even in concentrated acids. A solution of ammonium oxalate dissolves only traces of yttrium oxalate, but erbium oxalate dissolves in it with great readiness, forming a well-defined crystallisable double salt.

#### Erbium Salts.

Chloride . . . . .	$\text{ErCl}^2 + 4\text{H}^2\text{O}$
Bromide . . . . .	$\text{ErBr}^2 + \text{H}^2\text{O}$
Sulphocyanate . . . . .	$\text{Er}(\text{CNS})^2 + 4\text{H}^2\text{O}$
Chlorate . . . . .	$\text{Er}(\text{ClO}^3)^2 + 6\text{H}^2\text{O}$ (?)
Iodate . . . . .	$\text{Er}(\text{IO}^3)^2 + 2\text{H}^2\text{O}$
Sulphate . . . . .	$(\text{ErSO}^4)^2 + 8\text{H}^2\text{O}$
Selenite . . . . .	$\text{Er}^2\text{H}^4(\text{SeO}^3)^4 + 3\text{H}^2\text{O}$
Pyrophosphate . . . . .	$\text{Er}^2\text{H}^2(\text{P}^2\text{O}^7)^2 + 7\text{H}^2\text{O}$
Acetate . . . . .	$\text{Er}(\text{C}^2\text{H}^3\text{O}^2)^2 + 3\text{H}^2\text{O}$
Succinate . . . . .	$(\text{ErC}^2\text{H}^3\text{O}^4)^2 + 3\text{H}^2\text{O}$
Double potassium sulphate . . . . .	$\text{ErK}^2(\text{SO}^4)^2$
" potassium oxalate . . . . .	$\text{Er}^2\text{K}^2(\text{C}^2\text{O}^4)^7 + 12\text{H}^2\text{O}$
" ammonium oxalate . . . . .	$\text{Er}(\text{NH}^4)^2(\text{C}^2\text{O}^4)^4 + 5\text{H}^2\text{O}$
Fluoride . . . . .	$\text{ErF}^3$
Ferrocyanide . . . . .	$\text{K}^2\text{Er}^2\text{C}_6\text{Fe}^2 + x\text{H}^2\text{O}$
Nitrate . . . . .	$\text{Er}(\text{NO}^3)^3 + 4\text{H}^2\text{O}$
Bromate . . . . .	$\text{Er}(\text{BrO}^3)^3 + 6\text{H}^2\text{O}$
Periodate . . . . .	$\text{Er}^2\text{I}^2\text{O}^8 + 2\text{H}^2\text{O}$
Sulphite . . . . .	$\text{ErSO}^3 + \text{H}^2\text{O}$
Orthophosphate . . . . .	$\text{Er}^2(\text{PO}^4)^3 + 2\text{H}^2\text{O}$
Carbonate . . . . .	$\text{Er}^2 \begin{pmatrix} \text{OH} \\ (\text{CO}^3)^2 + \text{H}^2\text{O} \\ \text{OH} \end{pmatrix}$
Oxalate . . . . .	$\text{ErC}^2\text{O}^4 + 2\text{H}^2\text{O}$
Platinocyanide . . . . .	$\text{Er}(\text{CN})^4\text{Pt} + 7\text{H}^2\text{O}$

Since most of the salts of yttrium and erbium contain the same quantity of water of crystallisation as the corresponding salts of magnesium and zinc, and since the sulphates are isomorphous with cadmium sulphate, it is probable that these elements might be arranged in the same series as magnesium and its congeners; but it will be noticed that they do not give the double sulphates so characteristic of the magnesium

series,  $R'R''(SO_4)_2 + 6H_2O$ . In addition to this, yttrium and cerium enter into numerous combinations with a triple atomic weight, which would seem to imply that they are trivalent elements. The question cannot as yet be settled by the specific heat of the metals, as they have not been obtained in the pure state.

**YTTROCERITE.** The composition of this mineral, according to two analyses by Rammelsberg (*Deut. Chem. Ges. Ber.* iii. 657), is:

CaO	CeO <sup>o</sup>	YO	Loss by ignition	Sp. gr.
47.27	9.35	14.87	2.52	3.863
49.32	16.14		undetermined	undetermined

From these numbers (with the atomic weights Ce = 92; Y = 64) Rammelsberg deduces the formula  $2(CaF_2.2YF_2.9CaF_2) + 3H_2O$ .

The ceroso-ceric oxide contained nearly half its weight of lanthanum and didymium oxides, and the substance designated by YO contained 30 p.c. of a base precipitable by barium carbonate and 70 p.c. of a base not thus precipitable.

**YTTROTANTALITE.** See TANTALATES (p. 1146).

## Z

**ZEONERITE.** See URANIC ARSENATES (p. 1190).

**ZINC.** *Atomic Weight, 65.*—*Preparation.*—Pure zinc may be prepared by the electrolysis of an ammoniacal solution of zinc sulphate, a zinc plate being used as the positive, and a T-shaped copper wire as the negative electrode. On passing the current of two Bunsen's elements through the liquid, crystals of zinc form at the ends of the T; they may be removed with a pair of forceps, and washed with dilute ammonia (J. Myers, *Compt. rend.* lxxiv. 196).

On the *Heat of Oxidation of Zinc*, see HEAT (p. 617).

On the action of Zinc on *Nitric acid* and on mixtures of this acid with *Hydrochloric and Sulphuric acids*, the ultimate products of which are Ammonia and Sulphate, Nitrate or Chloride of Zinc, see H. Sainte-Claire Deville (*Compt. rend.* lxx. 20, 580; *Jahresb. f. Chem.* 1870, 20).

On the action of Zinc on *Sulphurous acid*, see SULPHUR-ACIDS (p. 1134).

*Estimation of Zinc.*—J. H. Talbott (*Chem. News*, xxii. 229) precipitates the zinc from a hot neutral or nearly neutral solution with *sulphide of sodium* or *ammonium*, avoiding the use of a great excess. The precipitate then becomes very dense, especially after further boiling, and settles down quickly. After washing and drying it is ignited with free access of air, in a porcelain crucible, first gently, and afterwards very strongly, whereby, especially on addition of a few lumps of ammonium carbonate, pure zinc oxide is obtained.

In the *volumetric estimation* of zinc by solution of sodium sulphide, A. Deuss (*Zeitschr. anal. Chem.* ix. 367; *Jahresb. f. Chem.* 1870, 1002) recommends, as a delicate indicator of the termination of the reaction, paper saturated with *cobalt chloride*. On moistening this paper with the zinc solution, before the titration is complete, a white circle is formed, pale blue on the circumference; but if the slightest excess of sodium sulphide is present, a dark sharply defined colour is produced in the middle of the ring, as soon as the paper has absorbed the drop. The test-papers are prepared by saturating strips of filter-paper  $2\frac{1}{4}$  inches broad, and 10 to 12 inches long, with a solution of cobalt chloride containing 0.35 gm. CoO in 100 c.c.

Hugo Tamm (*Chem. News*, xxiv. 148) estimates zinc by treating the solution with *ammonia* till the precipitate first formed is redissolved, then adding hydrochloric acid to acid reaction, and precipitating with ordinary *sodium phosphate*. A bulky precipitate of zinc phosphate is thereby produced, which quickly settles down after boiling for a short time, and may be easily filtered and washed. After drying at  $100^\circ$  it has the formula  $Zn(NH_4)PO_4$ . At a red heat it is converted into pyrophosphate,  $Zn_2P_2O_7$ , but as the ignition is attended with some loss of zinc, it is better to calculate the zinc from the weight of the precipitate dried at  $100^\circ$ . The precipitation of the zinc is complete when the supernatant liquid is no longer clouded on addition of

sodium phosphate, but it is best to add at once a quantity of the reagent sufficient to produce a slight alkaline reaction, and then to leave the liquid in a warm place for 10-12 hours. It must also be observed that the precipitated zinc phosphide is not quite insoluble in water, and is apt to stick to the sides of the vessel. In estimating zinc by this method, it is necessary to ensure the absence of cobalt, nickel, manganese, calcium, and magnesium, and it is advisable to test the purity of the precipitate by a qualitative examination.

On the Estimation of Zinc in Blends, see A. Julien (*Chem. News*, xxv. 16; *Jahresb. f. Chem.* 1872, 911).

On the Separation of Zinc from Lead, see p. 726 of this volume; from Nickel, p. 849.

**Zinc Iodide,  $ZnI_2$ .** Compounds of this iodide with aniline and toluidine are obtained by mixing the two bodies in alcoholic solution. The compounds,  $2C_6H_5N.ZnI_2$  and  $2C_6H_4N.ZnI_2$ , are both soluble in alcohol and crystallise in needles (H. Vohl, *Arch. Pharm.* [2], cxlviii. 201).

**Oxide,  $ZnO$ .** On the effect of Calcination on the Heat evolved in the solution of this oxide in acids, see HEAT (p. 617).

On the Change of Colour produced in Zinc Oxide by Heat, see LIGHT (p. 747).

**Phosphide.** A zinc phosphide, probably having the composition  $ZnHP$ , is formed by passing phosphine gas into a well-cooled ethereal solution of zinc-ethyl (Drechsel a. Finkelstein, *Zeitschr. f. Chem.* [2], vii. 375). On the Formation of Organic Phosphines by the action of this compound on Iodide of Ethyl, &c., see PHOSPHINES (p. 951).

**Sulphide,  $ZnS$ .** According to A. Wagner (*Dingl. pol. J.* cxvii. 334) the formation of this compound by passing hydrogen sulphide over air-dried zinc hydrate takes place very slowly. When the sulphide thus formed is exposed to the air, it continues to give off hydrogen sulphide, and reproduces zinc oxide even after three months, this result being due, not to the action of carbonic oxide, which, according to Wagner, does not decompose sulphide of zinc, but to a reaction of the zinc sulphide with water.

On the crystalline form of native Zinc Sulphide (blende), see Sadebeck (*Jahrb. f. Mineralogie*, 1870, 224; 1872, 644; *Jahresb. f. Chem.* 1869, 1194; 1872, 1093); and Klein (*Jahresb.* 1871, 1126; 1872, 1093).

Zinc blende is decomposed by iodine only at high temperatures, best at  $200^\circ$ ; in presence of water a small quantity of sulphate is formed (Fihol a. Molhies, *Ann. Chim. Phys.* [4], xxii. 58); also v. Lasaulx (*Jahresb. f. Chem.* 1870, 1272).

On the Roasting of Argentiferous Blendes, see Simonet (*Ann. Min.* [6], xvii. 27; *Jahresb.* 1870, 1085).

**ZINC-GREEN.** Green pigments are obtained by mixing zinc oxide with cobalt sulphate, boiling with water, drying, and heating the residue to redness. 5 pts. zinc oxide and 1 pt. cobalt sulphate yield a dark green; 10 pts. zinc oxide and 1 pt. cobalt sulphate a grass-green, the colour becoming still lighter when the quantity of zinc oxide is again doubled. The latter colour may be used as a substitute for Schweinfurt green, and as a coating for plaster.

**ZINC-SPAR.** A massive zinc-spar from Raibl in Carinthia was found by E. Ludwig (*Min. Mitt.* 1871, 55) to contain:

$CO_2$	$SiO_2$	$ZnO$	$FeO$	$H_2O$	
31.32	0.27	59.59	7.42	1.44	= 1000.04

**Iron-Zinc-spar.**—A greyish indistinctly schistose mass from Ain Saffre, province of Constantine, Algeria, is regarded by Flajolot (*Ann. Min.* [6], xx. 36) as an argillaceous variety of iron-zinc-spar. Analysis gave:

$ZnCO_3$	$FeCO_3$	$MnCO_3$	$CaCO_3$	$MgCO_3$	Clay
43.05	28.60	5.10	2.05	2.10	19.20 = 100.

**ZIRCON.** This mineral is found in the hyperstheneite of the Radey valley near Hamburg, in very small crystals of the combination  $\infty P.P.SP_3$ , of a white to reddish-white colour, and strong adamantine lustre. The zircon, which is imbedded for the most part in labradorite, resembles in every respect that which is found in such abundance in the gold sand of Columbia, and sparsely in the gold sand of the Grails, and renders it highly probable that both these zircons are from a matrix similar to the Harts rock (Gustav Rose, *Jahrb. f. Min.* 1871, 77).

The following analyses of zircons are by H. Cochrane (*Chem. News*, xxy. 408).

1. Ceylon, colourless; 2. Ceylon, yellowish; 3. Norway, dark yellowish; 4 and 5. Ceylon, colourless; 6. Norway, dark yellow-brown; 7. Ceylon, reddish-brown.

SiO <sup>2</sup>	33.90	32.87	32.53	33.05	33.86	33.61	33.81
ZrO <sup>2</sup>	64.80	64.25	64.05	66.71	64.25	64.40	66.32
Fe <sup>2</sup> O <sup>3</sup>	—	2.04	2.85	trace	1.08	0.90	trace
	98.70	99.16	99.43	99.76	99.19	98.91	100.13

A. H. Church (*Chem. News*, xxiii. 78) describes zircons (hyacinths) from Mudjee in New South Wales. Sp. gr. = 4.704; after ignition, attended with decoloration, 4.699.

The remarkable black bands in the spectra of certain zircons, now known to be due to the presence of certain compounds of zirconia with uranic oxide (1st Suppl. 1135), were first observed by Church in 1866 (*Chem. News*, xix. 121).

**ZIRCONIA**, ZrO<sup>2</sup>. B. Franz (*Deut. Chem. Ges. Ber.* iii. 58) prepares this earth by fusing zircon with acid potassium sulphate, and lixiviating the pulverised melt with boiling water acidulated with sulphuric acid, whereby the basic sulphate, 3ZrO<sup>2</sup>.SO<sup>3</sup>, is obtained as insoluble residuo. This salt is added by small portions to melting sodium hydrate; the melt is lixiviated with cold water; and the undissolved zirconia, still contaminated with soda, is dissolved in hot strong sulphuric acid, filtered and precipitated by ammonia.

Zirconia crystallises from fused phosphorus salt in combinations of the quadratio system,  $\infty$ P.O.P, very much like cubes. From fused borax, zirconia crystallises in rather large well-defined, transparent, colourless, many-faced crystals, formed of a primary prism, a pinacoid parallel to the principal axis, and two domes. The dome normal to the vertical pinacoid forms an angle of 90°. A brilliant coloured polarisation is seen in the direction normal to the pinacoid. Sp. gr. = 5.42 (Knop, *Ann. Ch. Pharm.* clvii. 363; *Jahresb.* 1871, 322; *Chem. Soc. J.* [2], ix. 804).

**ZIRCONIUM**. Metallic zirconium prepared by Troost's process from the pure zirconia above described, exhibited the properties mentioned in vol. v. p. 1080.

On the Detection and Estimation of Zirconium in Tantalates and Niobates, see Rammelsberg (*Chem. Soc. J.* [2], x. 195).

**Zirconium Bromide**, ZrBr<sup>4</sup>, may be prepared by mixing zirconia with excess of pure sugar-charcoal, forming the mixture into balls with starch-paste, drying them, and heating them to bright redness in a current of carbon dioxide and bromine-vapour. It is a white powder, which appears crystalline under the microscope, volatilises easily at the heat of a gas-burner, and is not reduced to a lower bromide by ignition in a stream of hydrogen. In contact with water (or moist air) it is converted into the oxybromide, ZrBr<sup>3</sup>O, which separates from aqueous solution in fine transparent, needle-shaped crystals (Melliss, *Zeitschr. f. Chem.* [2], vi. 196).

**Zirconium Chloride**, ZrCl<sup>4</sup>, is formed by the action of silicium chloride in the form of vapour on zirconia (Troost & Hautesfeuille, *Compt. rend.* lxxv. 1819).

The oxychloride, ZrOCl<sup>2</sup>, obtained by Hermann (v. 1080), crystallises, according to Melliss, not with 9H<sup>2</sup>O, but with 4½H<sup>2</sup>O.

**Compounds of Zirconium with Aluminium and Silicon.** 1. When 1 pt. of pulverised zircon is heated to whiteness with 5 pts. of cryolite powder, 1 pt. of aluminium, and 10 pts. of a mixture of the chlorides of potassium and sodium, an aluminium regulus is obtained, which, when treated with dilute hydrochloric acid, yields, together with finely-divided crystalline and darker-coloured silicon, laminar and proportionally large crystals, which may be separated from the silicon by elutriation. These crystals have the composition ZrAl<sup>3</sup>, or, if the silicon (6.72 p.c.) found in their hydrochloric acid solution be regarded as a third constituent, they may be represented by the formula Zr<sup>2</sup>Al<sup>3</sup>Si.

When zircon is fused with sodium carbonate, and the fused mass is exhausted with hot water, a residuo is obtained consisting of the compound 8ZrO<sup>2</sup>.SiO<sup>2</sup>.Na<sup>2</sup>O + 11H<sup>2</sup>O. Potassium carbonate yields in like manner the compound ZrO<sup>2</sup>.K<sup>2</sup>O.2SiO<sup>2</sup>, or ZrSiO<sup>4</sup>.K<sup>2</sup>SiO<sup>2</sup> (Melliss, *Zeitschr. f. Chem.* [2], vi. 296).

**ZIRLITE**. A hydrate of alumina from Zirl in the Tyrol (Pichler, *Jahrb. f. Min.* 1871, 67).

END OF THE SECOND SUPPLEMENT.









